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THE PNEUMATOLYTIC AND HYDROTHERMAL ALTERATION AND SYNTHESIS OF SILICATES.

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THE study of the conditions of mineral formation has been carried out principally by two methods, the fusion method and the hydrothermal method. A large part of the work of the Geophysical Laboratory has been devoted to the study of silicate systems under their own—usually inappreciable—vapor pressure. As the result of this work there is now a comprehensive knowledge of the fundamental phase equilibrium relationships of the two- and three-component systems which have a direct bearing on the formation of igneous rocks, and much, though far from complete, information as to the more complex systems.

Our knowledge of systems containing a volatile component under the vapor pressure corresponding to coexistence of vapor, liquid and solid phases is far less comprehensive. Most of the papers cited in this review chronicle only the synthesis of certain silicate minerals by heating their components with water in closed vessels, at temperatures from the boiling point to above the critical temperature of water, and at the pressure of water vapor determined by the temperature and the nature and concentration of the components. In a large proportion of cases those factors are not given. There has been almost no attempt to develop systematic equilibrium data. Frequently several different inhomogeneous materials have been mixed together in a given experiment, producing

multi-component systems of such complexity that systematic knowledge could not be obtained from them. Almost without exception, the experiments have been made under conditions which were not carefully controlled, and under which equilibrium could not be attained, and hence give no knowledge concerning the solubility or fusion relationships in the aqueous systems.

The time is past in which the artificial production of a mineral, even by hydrothermal methods, is of more than passing interest. There is need for the development of systematic information leading to a knowledge of the part played by water in silicate equilibria; of the phase-equilibrium relationships in systems containing both water and silicates. Only in this way can the problems of magmatic differentiation, of pegmatite formation, of metamorphism, as well as of mineral concentration and deposition, be solved. Such a program is difficult, but to attempt it is a necessary step in the application of physico-chemical methods to the problems of geology.

In this review, the authors have attempted to include all papers, and to give in abstract all data, which relate to the actual identification of certain minerals or are important because of the conditions under which the product was obtained. While it is believed that all the important papers have been included, no attempt has been made to search technical journals devoted to industries such as pottery or cement manufacture. It is also possible that some work has been overlooked because it appeared in papers dealing with topics apparently unrelated to the subject in hand. It formed no part of the authors' purpose to include papers dealing with mineral syntheses by means of superheated steam in open vessels (*e.g.* the work of Meunier),[1] or papers, such as those of Zambonini,[2] on the loss of water by minerals above 100°.

[1] Meunier, S.: Les Méthodes de Synthèse en Minéralogie. Paris, 1891.

[2] Zambonini, F.: Mem. accad. Lincei, Classe sci. fis. mat. nat., [5], vol. 5, pp. 343–374, 1904–05. Rome; vol. 6, pp. 101–127, 1906.

THE EXPERIMENTAL METHODS.

The study of hydrothermal processes is the study of certain aqueous systems at high temperatures, approaching and above the critical temperature of water, and therefore under the very considerable pressures developed at these temperatures by pure water or aqueous solutions. There is now available a substantial body of experimental data on the properties of water both below and above its critical point. These data include the work of Keyes and his associates,[3] and the data of van Nieuwenburg and Blumendal.[4]

The experimental difficulties in the study of aqueous solutions at high temperatures and pressures are many, but are largely connected with the choice of suitable containing vessels and the exact control of the conditions of working. The high pressures developed, and the solvent action of water at high temperatures preclude the general use of glass vessels except in special cases. Daubrée (5),[5] to be sure, used glass tubes, minimizing the effect of pressure by placing the glass tubes inside closed steel tubes with water in the annular space between. Chroustschoff (48) also used glass tubes at temperatures up to 550°, but does not mention taking the above precaution. Both Daubrée and Chroustschoff found that the glass was much attacked, but this was of no great moment to them, as they were concerned only with obtaining a product corresponding to some known mineral.

Most of the investigators have used vessels of steel, made tight in an appropriate manner. Perhaps the simplest form is that used by Senarmont (3) and later by Doelter (43), namely, a gun-barrel closed by a screw-cap and copper washer. With this apparatus, however, as with many of the older forms, experimental uncertainties were introduced by the lack

[3] Keyes, F. G.: Proc. Am. Acad. Arts Sci., vol. 68, p. 505, 1933; Smith, L. B., Keyes, F. G., and Gerry, H. T.:I dem., vol. 69, p. 137, 1934; Smith, L. B., and Keyes, F. G.: Idem., vol. 69, p. 285, 1934; Keyes, F. G., Smith, L. B., and Gerry, H. T.: Idem., vol. 70, p. 319, 1936.

[4] Van Nieuwenburg, C. J., and Blumendal, H. B.: Rec. trav. chim., vol. 51, p. 708, 1932.

[5] These numbers refer to the number of the paper in the bibliographical list (p. 639).

of a perfectly tight closure, the leak allowing a part, or even all, of the water to escape and thereby causing variations of the pressure, and hence of the concentration, of the water in the course of the experiment.

Friedel and Sarasin (19, 23) used in much of their work a steel tube closed at each end by a cap held tight by bolts, the joint being made tight by means of an iron disc bearing a copper washer. Doelter,[6] however, who also used a similar tube, states that it is serviceable only when very carefully bolted together, and even then only up to about 450°; further, that it ceases to be serviceable after being used a few times.

Baur (78) used a bomb consisting of a steel cylinder, bored out to receive the charge and cover, the latter being a plug screwed into the top of the bore and made tight by means of a copper washer. Morey and Fenner (89) devised a pressure-tight bomb which has been used by other investigators, embodying principles which have been adopted in most high-pressure work. The bomb is a cylinder of tool steel, bored out and fitted with a screw-plug, and a plunger which fits against a shoulder. The seal is made tight by placing an annealed copper washer between the plunger and shoulder. The plunger should be a close fit in the recess allowed for it, and a part should project into the body of the bomb, thus imprisoning the copper washer and preventing flow at high temperature and pressure. A slip-washer should be placed between the plunger and the screw-plug. The provision of a separate unit to apply to the washer the pressure developed by the screw is essential in order to avoid a shearing moment on the copper seal.

An interesting development was made by Königsberger and Müller (75), who introduced a filtering apparatus of platinum, enabling the separation of the solid from the solution at any temperature. It was not widely adopted. Other investigators, usually working at lower temperatures and pressures, have devised apparatus to achieve the same result. Of interest in this connection is the apparatus of Waldeck, Lynn

[6] Handbuch Mineralchemie, vol. 1, p. 616, 1912.

and Hill,[7] with which they studied the solubility in water of sodium carbonate up to 348°. Similar methods have been used by Schroeder and co-workers,[8] Straub (153), Hitchen (139), and Norton (156).

On account of the action of many solutions on the iron of the bombs, many experimenters have used linings of more resistant metals, such as silver, gold or platinum. Baur, however (78), considers a lining unnecessary, stating that the action on the iron is negligible by reason of the formation of a protective coating of ferrous-ferric oxide. It is undoubtedly true that with neutral solutions the action is slight, but when acid or strongly alkaline solutions are used their solvent action is no longer negligible, and the products obtained are often contaminated by considerable quantities of iron. Indeed, when the iron is corroded to any great extent, the mineral associations may be greatly altered, in which case the products obtained will probably be essentially different from those obtained when the charge is kept free from this component, which often exercises such a profound effect on the final character of the system. While, in the opinion of the authors, lining the bomb with a noble metal is not necessary, still it is advisable that the charge should be placed in a separate container made of gold or platinum. Our experience under such conditions has shown that although the bomb itself may be quite strongly attacked, the contents of the crucible rarely show any appreciable contamination.

THEORETICAL PRINCIPLES UNDERLYING HYDROTHERMAL PROCESSES.

Before discussing the general results of the experiments abstracted in the bibliography, we shall consider the basic physico-chemical principles of hydrothermal processes. An

[7] Waldeck, W. F., Lynn, G., and Hill, A. E.: J. Am. Chem. Soc., vol. 54, p. 928, 1932; vol. 56, p. 43, 1934.

[8] Schroeder, W. C., Gabriel, A., and Partridge, E. P.: J. Am. Chem. Soc., vol. 57, p. 1539, 1935; and Schroeder, W. C., Berk, A. A., and Gabriel, A.: J. Am. Chem. Soc., vol. 58, p. 843, 1936.

exhaustive treatment will not be given, because, on the one hand, the experimental data are too scanty to afford examples of the application of the principles involved, and because, on the other hand, many of these principles have been treated in detail in other places.[9, 10, 11]

Though the mechanisms of the reactions are often complicated, all hydrothermal syntheses are, primarily, crystallizations from aqueous solutions. As such they are comparable with van't Hoff's researches on the oceanic salt deposits, the differences being only in the magnitude of the temperature, pressure and composition (concentration ratios); the differences in the actual experiment are of course more marked owing to the intervention, at the high temperatures, of certain disturbing factors. The principles involved, however, are not altered by the circumstance that under the special conditions involved, the concentrations may by reason of small specific solubilities be very small, and that the concentration of the solvent itself may be so slight that it has the properties of a gas, since above the critical temperature the concentration of the water is dependent upon the pressure prevailing. The associations of the minerals obtained are primarily and essentially those in the presence of aqueous solutions, and, as such, are to be differentiated from the associations of the same water-free compounds obtained from the dry melt, or in the presence of solvents other than pure water.

[9] Smits, A.: Zeit. Elektrochem., vol. 9, p. 663, 1903; Zeit. physik. Chem., vol. 51, p. 193, 1905; vol. 52, p. 587, 1905; vol. 54, p. 498, 1906; vol. 54, p. 513, 1906; vol. 67, p. 454, 1909; vol. 67, p. 464, 1909; vol. 76, p. 445, 1911. Also in Proc. Koninkl. Akad. Wetenschappen Amsterdam, vol. 13, p. 342, 1910; vol. 15, p. 184, 1912; vol. 18, p. 793, 1915.

Niggli, P.: Zeit. anorg. Chem., vol. 75, p. 161, 1912; vol. 77, p. 321, 1912; Centr. Min., 1912, pp. 321–338; Neues Jahrb., vol. II, p. 69, 1914.

[10] Morey, G. W., and Niggli, P.: J. Am. Chem. Soc., vol. 35, p. 1086, 1913. This paper contains an annotated bibliography, complete up to the date of printing, some of which has been reproduced in this review, with alterations, amplifications and additions.

[11] Morey, G. W.: J. Wash. Acad. Sci., vol. 12, p. 219, 1922; J. Geol., vol. 32, p. 291, 1924.

The form of the solubility or fusion [12] curves of systems, made up of components whose melting points do not lie far apart, is determined by simple and well-known physico-chemical principles; but in hydrothermal systems the fact that the critical point of one component is at a temperature much lower than the melting point of the other introduces disturbing complications, which render the theoretical treatment of these curves less simple. There is no doubt that silicates are soluble in water, though in many cases only with decomposition, and also that fused silicates may, under appropriate conditions, hold water vapor in solution; in other words, we know the general course of a fractional portion of the solubility curve close to each pure component. What we wish to determine is the general course of the whole curve.

Now, in the T-X projection of the phase equilibrium diagram for a binary system, the triple points [13] of the two components are joined by the solubility or fusion curve; the melting points involved are those determined by the prevalent temperature and concentration. It may, of course, happen that part of this curve lies in a metastable region, especially if transformations take place or if the two components are but partially miscible. Just as the triple points are joined by a single continuous solubility or fusion curve (which gives the composition of the liquid coexisting in equilibrium with vapor), so also are the critical points of two substances joined by a critical curve.[14] In this case also a part of the curve may lie outside the stable region, if transformation, decomposition, or limited miscibility occur. The different possible cases which can be logically considered, are two:

I. The solubility curve does not intersect the critical curve (Fig. 1).

II. The solubility curve intersects the critical curve (Fig. 2).

[12] The processes of solution and of fusion are in principle identical.

[13] The triple point is the melting point of the substance under its own vapor pressure at that temperature; it is practically the same as the ordinary melting point (at a pressure of 1 atm.) since the variation of melting point with pressure is very small.

[14] That is, the plait curve which represents the locus of all points where the critical phenomena occur with mixtures intermediate between the pure components.

Figure 1 is a diagrammatic representation of one of the possible phase equilibrium diagrams included under Case 1. Since the critical points of the components lie at much higher values of temperature and pressure than the corresponding melting points, it follows that, when the solubility and critical curves do not intersect, the solubility curve must be below the corresponding critical curve. Moreover, the two-phase line in coexistence with solid (solid-solution-vapor) must also be below the critical curve. Hence, on the one hand, only unsaturated solutions will show critical phenomena, and, on the other hand, the two-phase line in coexistence with solid phase can be studied without the appearance of critical phenomena. The critical point of the more volatile component is in this case without influence in the solubility relations solid-liquid or solid-vapor. In the system water-silicate we can therefore expect, provided that complications are not introduced by decomposition or limited miscibility, that a continuous two-phase line in coexistence with solid will connect the melting point of ice with the melting point of the silicate. At high pressures, a homogeneous liquid mixture will probably be formed at relatively lower temperatures, since the melting point of the silicate will be lowered throughout the whole concentration range by liquid water. Examples of such continuous solubility curves are the binary systems, H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$ (89), shown in Fig. 10.

Conditions are very different in the second case. Since, in mixtures approaching in composition either one of the pure components, the two-phase line coexisting with solid must be below the critical curve, it follows that, when the critical curve is intersected in one point by the solubility curve, it must also be intersected in a second point. The two intersections are characterized by the fact that while at these points the critical phenomena are shown by solutions in contact with solid phase (saturated solutions) between these points the critical phenomena can only take place in supersaturated (metastable) solutions. Above the upper, and below the lower, critical end point, the three phases solid-

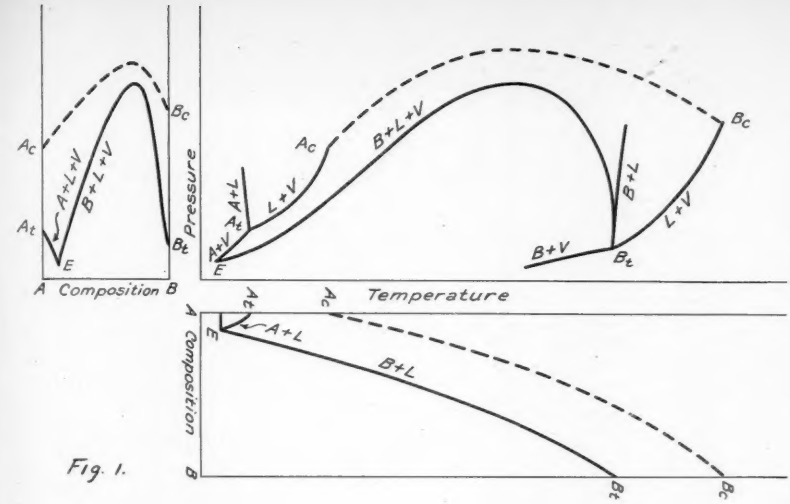


Fig. 1.

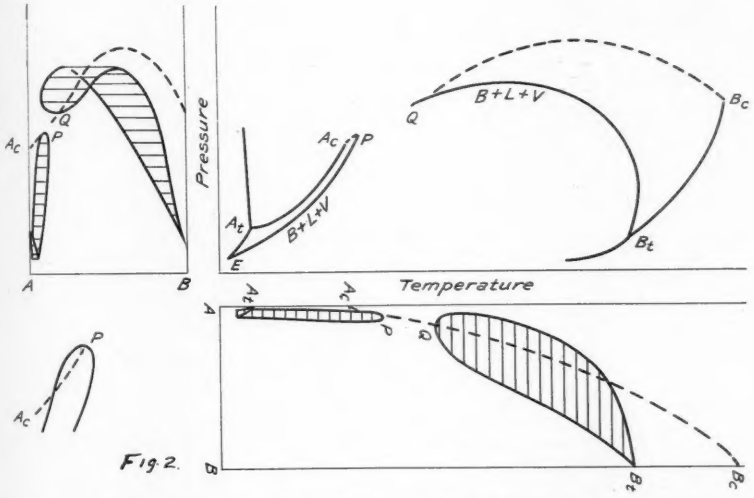


Fig. 2.

FIGS. 1 AND 2. Projections on the temperature-concentration, temperature-pressure, and pressure-concentration planes of a solid model which gives a diagrammatic representation of the phase equilibrium relationships in a binary system with components of widely different volatility, in which the critical or plait point curve in Fig. 1 (upper) *is not* intersected by the solubility curve. A_t and A_c, and B_t and B_c, represent the triple and critical points for the two components, respectively. E is the binary eutectic.

In Fig. 2 (lower) the critical curve *is* intersected by the solubility curve. The tie-lines connect co-existing vapor and liquid compositions. The lower critical end-point is at P; the upper, at Q; otherwise symbols are as in Fig. 1.

liquid-vapor can coexist; but in the field between them the only stable phases are solid and fluid (gaseous) solutions, and there will not be a continuous line representing two-phase equilibria in the presence of solid phase. This circumstance has the following consequences, which have a very important bearing on the experimental side of our problem.

In the field below the first critical end point, at a given volume and with a moderate amount of water, the state of the system will be completely determined by the temperature alone. Moreover, variation within certain limits of the amount of water, provided that the temperature is constant and that stable equilibrium is attained, is without effect on the final vapor pressure or on the concentration of either the saturated vapor or saturated solution; the only effect of such variation (the total volume remaining always the same) is to change the relative amounts of vapor and liquid solution. In the field between the two critical end points the conditions are very different. Here we have a two-component system, and only two phases, solid and fluid solution. The system is therefore divariant; at given temperature and volume a small change in the amount of water will result in a change of pressure, hence of concentration of the vapor phase. It is evident that in this region the possibility of obtaining various minerals is greater, and, conversely, that within this region it is a more difficult matter to reproduce exactly a set of experimental conditions. Several cases may be distinguished in which the critical curve is intersected by the solubility curve. For example, the intersection may take place below the maximum pressure, as shown in Fig. 2, or at a temperature higher than corresponds to the maximum pressure. The formation of compounds, which may have either congruent or incongruent melting points, gives rise to special cases. The alterations in the diagrams thus made necessary are evident.

The occurrence of cases of the second type is evidently dependent on the following conditions: First, the volatility of the two components must be very different; second, the

solubility of the less volatile component in the more volatile component must be small near the critical point of the latter. The critical temperature and pressure of a substance are raised by a dissolved substance; this elevation of the critical temperature is analogous to the elevation of boiling point, and is, according to Centnerszwer, in dilute solutions, proportional to the mol fraction of the solute.

If, at the critical point of water, 374° and 218 atmospheres, the solubility of a silicate is very small, the saturated solution will show critical phenomena [15] at a temperature and pressure very little above the values for pure water. It follows, as we have seen, that above this critical point there is a field in which the stable phases are two—fluid (gaseous) solution and solid. The stable coexistence of liquid and vapor in this region is impossible; but, on the other hand, the fluid phase is just as much a solution as the ordinary aqueous solutions in contact with vapor. The lack of outstanding distinction between liquid and fluid (gaseous) solutions can be shown indeed by an actual example; for at constant pressure the solubility curve for the system ether-anthraquinone, studied by Smits,[16] exhibits no discontinuity at the critical point of the more volatile component.

Hence we may say that, for cases of the second type also, the critical point is without direct influence on the solubility phenomena. This statement is, however, subject to some qualification in its quantitative aspect, the basis of which is the relatively rapid change of solubility which must occur in the immediate neighborhood of the critical point. At temperatures considerably below the critical point, the proportion of the less volatile component in the liquid phase is much greater than it is in the coexisting vapor phase; but as we approach the critical point the two solubilities approach one another, since at the critical point they are identical. In general, therefore, in the region shortly before the critical end point, the solubility in the vapor phase must increase, while that in

[15] Provided, of course, that the volume of the system has the appropriate value.

[16] Smits, A.: Proc. Koninkl. Akad. Wetenschappen Amsterdam, 1911, p. 191. See Figs. 3. 4 and 5, taken from Smits, A.: Zeit. physik. Chem., vol. 52, pp. 587–601, 1905.

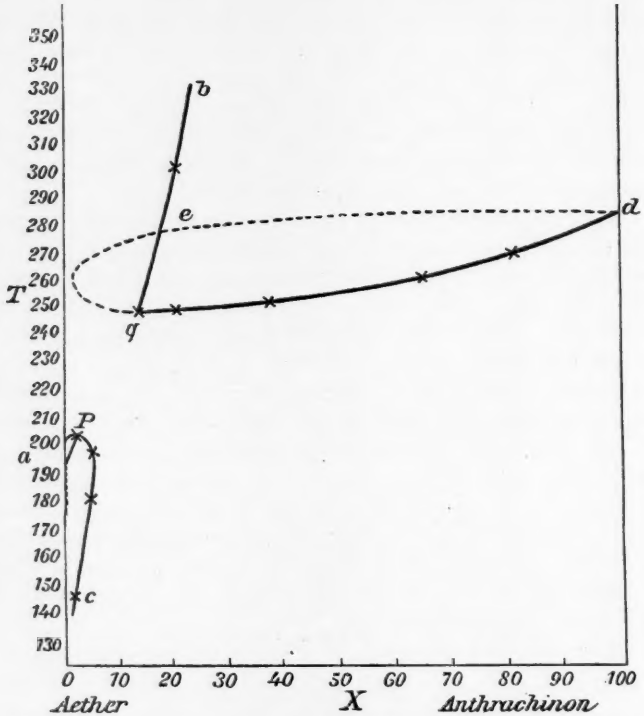


FIG. 3. Temperature-concentration diagram for the binary system ether-anthraquinone. After Smits. The curves *Pc* and *aP* represent respectively the liquid and vapor phases below the first critical end-point, *P*. The curve *dq* is the upper part of the solubility curve, from the melting point of anthraquinone, *d*, to the upper critical end-point, *q*; the dashed curve represents the co-existing vapors. The curve *qb* gives the critical temperatures of unsaturated solutions, ending at the saturation curve *dq*. Cf. Figs. 4 and 5.

the liquid phase must decrease.[17] This qualification depends upon a purely local, continuous and thermodynamically determinate phenomenon. It frequently happens that the

[17] The thermodynamic necessity of this has been proved by A. Smits, Proc. Koninkl. Akad. Wetenschappen Amsterdam, vol. 14, p. 170, 1911.

solubility is practically zero in both phases and the point is then a purely academic one.

The solubility curve goes from the melting point of one component to that of the other; from what has been said above it follows that the solubility (of the non-volatile component) in the fluid or (above the second critical end point) subsequent liquid phase will increase with increasing temperature, provided that the components are always completely miscible and that no exothermal reactions occur. In this connection we may remark that the concentration of the liquid is diminishing very rapidly as its critical point is approached, while the concentration of the vapor is rapidly increasing; and that the solubility, if it is reckoned as the concentration of solute in the total amount of solvent present in both liquid and vapor phases, need not diminish in the critical region in all cases, although we shall always have a retrogressive solubility curve if the liquid phase alone is considered.

Critical phenomena are of importance in laboratory experimentation, but it is doubtful if they can play more than an occasional part in magmatic phenomena.[18] The critical point of water is characteristic only of pure water, and the presence of any substance in solution will raise the critical temperature. As the cooling magma eliminates one component after another by crystallization, more or less completely, the residual magma probably will at all times contain enough material of lesser volatility, such as borates, phosphates, silico-fluorides, fluorides and chlorides, to hold the components of greater volatility, mainly water, in solution. In other words, it is probable that the critical phenomena are never shown by saturated solutions formed from the cooling magma, and the critical curve of these liquids is not cut by the solubility curve. The liquid magma at any stage would have to be heated to a higher temperature to show critical phenomena.

This failure to show critical phenomena applies only to primary magmatic solutions. It is possible that the dilute

[18] Morey, G. W.: J. Geol., vol. 32, p. 291, 1924.

emanations that have left the magma and condensed may show critical phenomena on re-heating. This situation is probably rare and unimportant in nature.

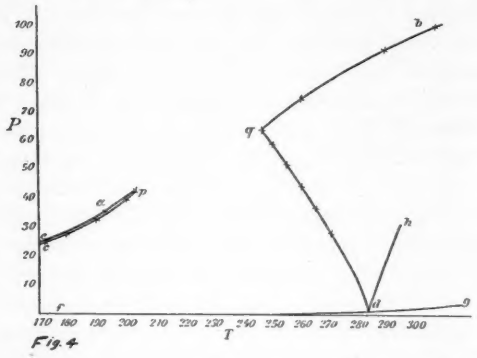
The emanations, however, considered as a separate system, are probably commonly in the supercritical state [19] when they leave the magma, although the original system (magma and vapor) has at no time exhibited critical phenomena. This fact may be of considerable geologic importance, since these highly compressed gases (mostly water) can serve as solvents of non-volatile matter, thereby providing a mechanism for transporting material from the magma without assuming the existence of intrinsically volatile compounds for which there is little or no evidence in nature.

The critical point, as such, has thus nothing to do with the solubility phenomena, nor with the nature of the solid phase, and Doelter [20] is in error in ascribing to the critical point of water a significant role in hydrothermal synthesis. That the formation of zeolites, or, more generally speaking, of minerals containing water, will be less common at high temperatures is evident, but this circumstance is caused by the increase of the dissociation pressure of such compounds with increasing temperature. The critical temperature of water is not only theoretically without effect on the phenomena in question, but, as a matter of fact, many hydrated minerals have been obtained under conditions such that we are led to conclude that they formed in presence of solutions which were fluid (not liquid).

As an illustration of some of these relations we reproduce the diagrams (Figs. 3, 4 and 5) given by Smits to exhibit the melting (solubility) lines at various pressures for the system ether-anthraquinone. This system has 2 critical end points; the first (P in Figs. 3, 4 and 5) at 203° and 39.7 atmospheres,

[19] For a more complete discussion of these extra-magmatic systems and the possible importance of their behavior in geologic processes see Ingerson, E.: Relation of critical and supercritical phenomena to geologic processes. ECON. GEOL., vol. 29, pp. 454–470, 1934.

[20] Handbuch Mineralchemie, vol. 1, p. 603, 1912; Phys. Chem. Mineralogie, p. 216, 1905.



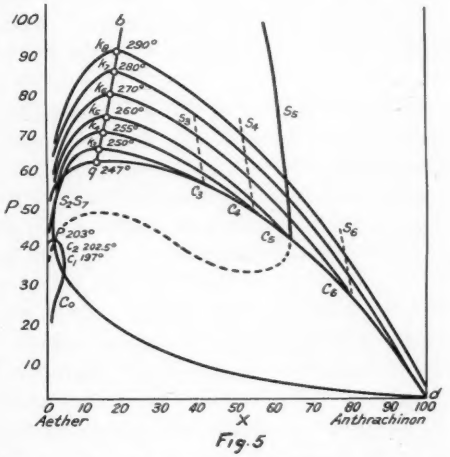


FIG. 4 (upper). Pressure-temperature diagram for the system ether-anthraquinone. After Smits. Curves *ep* and *qb* give the critical temperatures and pressures for unsaturated solutions, ending at the two branches of the solubility curve, *cp* and *dq*. Cf. Figs. 3 and 5.

FIG. 5 (lower). Pressure-composition diagram for the system ether-anthraquinone. After Smits. The curve $dC_6C_5C_4C_3q$ is the upper part of the solubility curve; *dq* gives the compositions of the co-existing vapor phases. The curves C_3K_3, C_4K_4, etc., extending on each side of the plait-point curve, $qK_3K_4K_5K_6K_7K_8b$, represent co-existing liquid and vapor phases unsaturated with solid.

the second (q) at 247° and 62 atmospheres. If a system solid-liquid-vapor is heated in a closed vessel, the temperature at which either the liquid or the vapor phase disappears is dependent upon the degree of filling, that is, upon the ratio of the amount of water to the volume of the containing vessel. The true critical point is reached only when, at this temperature, the amounts of liquid and vapor are the same (*i.e.*, at the critical volume). In all other cases the last drop of liquid or the last bubble of vapor will disappear at a temperature different from, and in general lower than, the true critical temperature, though the latter does not necessarily coincide with the maximum temperature. Curves showing the transition of the three-phase system solid-liquid-vapor to the two-phase system solid-fluid in its dependence upon the degree of filling have been discussed by Centnerszwer [21] and by Niggli.[22]

The influence of pressure in such systems may well be enlarged upon. So long as both liquid and vapor phases are present, the pressure developed is independent of the degree of filling, if the solutions are saturated; for a saturated solution has, at a definite temperature, a definite vapor pressure, and the only effect of varying the amount of solvent present will be to vary the relative amounts of the liquid and vapor phases. This is no longer true, however, when we pass from the three-phase system to the two-phase system fluid-solid. At a given total volume a change in the degree of filling now causes a change in concentration—that is, pressure—of the fluid phase; hence, as a direct consequence of Henry's law, the amount of the solid in solution in the fluid phase varies with the degree of filling.

From this the possibility is evident that in such systems, at temperatures above the critical temperature, different syntheses may be effected merely by varying the degree of filling. In all experiments at temperatures near or above

[21] Centnerszwer, M.: Zeit. physik. Chem., vol. 46, p. 427, 1903; vol. 54, p. 689, 1906; vol. 60, p. 441, 1907; vol. 61, p. 356, 1908; vol. 69, p. 81, 1909; vol. 72, p. 431, 1910.

[22] Niggli, P.: Zeit. anorg. Chem., vol. 75, p. 179, 1912.

400°, therefore, the degree of filling, or at least the exact amount of water present, should be expressly stated. When the amount of water at ordinary temperatures is very different from one-third of the volume of the container, the transition into the two-phase systems may take place at a much lower temperature, as stated above; and this circumstance must always be taken into account.

One condition for the occurrence of the second type (appearance of two critical end points) is that the solubility of the non-volatile component in the volatile component should be small near the critical point of the latter. Now it is established, as the result of many experiments, especially by Königsberger (75) that the solubility of many silicates in water about 370° is very small; so that there is every reason to believe that many systems silicate-water belong to this second category.

In most cases, indeed, the solubility is so very small that the first critical end point will be close to the critical point of water itself; the difference will, in general, probably be only of the order of magnitude of fractions of a degree. Systems with water, which belong to the first category, are given by a few silicates which are relatively soluble in water; an example is the system, H_2O-$K_2Si_2O_5$ (89).

A more usual case with the common silicate minerals is that in which the solubility is small, and critical phenomena are shown. Examples are many, of which H_2O-SiO_2 may be chosen. The second critical end point, which must exist if neither unmixing nor decomposition occurs, will in all probability lie at very high pressures. In no case has it been observed in systems containing water, and we have no experimental knowledge of the maximum pressures in systems containing water.

From the above it is evident that there is no essential difference between ordinary aqueous solutions at room temperature and systems silicate-water, at temperatures near, or even above, the critical point of water. From ordinary aqueous solutions a substance begins to separate as soon as

its saturation concentration (under the particular conditions) is reached. In precisely the same way the crystallization of stable minerals from aqueous systems containing several relatively non-volatile components will be determined by the relative insolubility of the possible forms. In this respect these hydrothermal syntheses are similar to the parageneses obtained by van't Hoff in his researches on the oceanic salt deposits, the main difference being that van't Hoff approached his saturation limits by evaporation of the solvent at constant temperature, while in hydrothermal work separation of material from solution would be effected by successive lowerings of temperature. The "solubilities" of minerals are, however, so very slight that one cannot obtain in this way products even in quantity sufficient for their certain identification; for instance Königsberger in his experiments (75) was able, in general, to identify only quartz.

But we can consider the problem from another point of view, namely, that the reactions take place largely in the solid phase. Many examples of such reactions are known; as an illustration, we may take the well-known fact of the growth of crystals at temperatures below their melting point.[23] In hydrothermal work, we introduce as solid phase a mixture of substances which is believed to be unstable in the presence of solution under the conditions of the experiment. Under such circumstances reactions will take place in the mass of the solid tending to produce the solid phase [24] which is stable under the particular conditions; and when the diminution of free energy accompanying these reactions is a maximum, the syntheses obtained will be identical with those obtained by actual crystallization from saturated solutions under the same conditions. But the solid phase is such a complex system that we cannot, *a priori*, assume that the material actually

[23] Cf. the "Sammelkristallisation" of Rinne and Böcke, Tschermak's Min. petr. Mitt., vol. 27, p. 393, 1908.

[24] These reactions in the solid phase take place presumably through layers of supersaturated solution in the immediate proximity of the particles constituting the solid phase.

produced is the stable phase, and as a matter of fact, many crystals have been obtained which are metastable under the conditions given. An excellent example is tridymite, which has been obtained in the hydrothermal way, though its range of stability at ordinary pressures is from 870°–1470°.

Since the products actually obtained in hydrothermal syntheses have not in general crystallized out of cooling supersaturated solutions, but are the result of reactions taking place in the mass of the solid phase, it is to be expected that many of the products obtained will be metastable.[25] It is not justifiable, however, to assume that all products of reactions in the solid phase are metastable; the tendency is always towards the formation of the stable product. Many circumstances, such as the reproducibility of the experimental results and also data from other sources, make it at least highly probable that in a large number of mineral syntheses the stable product has been obtained. Yet it seems to us altogether premature to draw a diagram representing what purports to be the stability fields for these complicated systems, when the facts are so insufficiently ascertained; such diagrams may be altogether misleading, especially to those who are unable to distinguish for themselves between experimentally ascertained facts and inferential assumptions.

The interpretation of the results of hydrothermal syntheses is hampered, moreover, by the fact that we do not know the exact temperature of formation of the products, since some relatively permanent crystals may separate while the temperature is actually being raised initially, or during the final cooling. This factor, however, seems to us to have been overrated, since the cooling may be made very rapid; moreover, minerals formed while the temperature is being raised, but metastable at the temperature of experiment, will be transformed into the stable form when held at constant temperature, unless the rate of transformation of such metastable products is very small.

[25] It is of course also possible for metastable products to crystallize out of saturated solutions.

The circumstance that the temperature and pressure have not been determined at all accurately in most of the syntheses hitherto made naturally makes it difficult to obtain a comprehensive view of the present status of the problem. Such difficulties, however, are purely experimental, and can be obviated by the use of suitable technique, *e.g.* temperatures can be measured with sufficient accuracy by placing the thermoelement in a small hole drilled longitudinally in the plunger of the bomb. Neither does the measurement of the pressure appear to be an experimental impossibility. It is often, at least for preliminary work, sufficient to know the temperature within a few degrees; it is more important to know accurately the degree of filling.

Hitherto we have considered systems composed of silicates and water only; systems in which special mineralizers such as carbon dioxide, hydrofluoric or hydrochloric acid, either as such or in the form of their salts, are absent. The addition of such mineralizers increases the number of volatile components and introduces a further complication caused by the specific effect of these additions on the dissociation equilibrium of the silicate.

In all cases the chief influence of the addition of mineralizers will be to change the solubility relations involved. For example, from an experiment of Königsberger and Müller (79) it appears that sodium carbonate precipitates orthoclase from solution. That addition of hydrochloric or hydrofluoric acid will have a marked effect on the solubility relations is self-evident, for such additions alter the nature of the solvent.

In general, very little is known in regard to the ionization relations in aqueous solutions at temperatures above about 300°. All experiments hitherto recorded show that increasing temperature is accompanied by a decrease in the degree of ionization, which for different salts of the same ionic type tends to approach the same value. Practically nothing is known in regard to the hydrolytic dissociation of silicates at such temperatures.

GENERAL DISCUSSION OF THE EXPERIMENTAL WORK ON HYDROTHERMAL AND PNEUMATOLYTIC SYNTHESES.

In a general consideration of the various hydrothermal and pneumatolytic syntheses, the principles outlined in the theoretical discussion above must be borne in mind. Unfortunately, there has been practically no systematic work in this field. The only quantitative work is that by Morey and Fenner (89) on the ternary system, H_2O-K_2SiO_3-SiO_2.

Some work that may be classified as semi-quantitative has been done from time to time. That is, some workers have varied the compositions of mixtures used more or less systematically, and recorded the crystalline phases obtained in each experiment, but have made no attempt to study the equilibrium relations in definite systems. Among such works may be mentioned those of Baur (71), (78); Königsberger and Müller (75), (91); Niggli (84); Niggli and Schlaepfer (85); Ewell and Insley (138); and Noll (141), (152), (155). In some of this work only the ratio of the solid components was varied, temperature and degree of filling remaining practically the same in a whole series of experiments. In other cases water was included as a variable component, and in still others temperature, pressure, and composition were varied more or less systematically.

In the vast majority of published accounts of hydrothermal and pneumatolytic synthesis and alteration of silicates the work has been most haphazard. In many instances temperatures, pressures, and concentrations are given roughly, if at all. Some of the experiments have been attempts to produce some particular mineral, or minerals, with little or no attention being paid to conditions of formation or ranges of stability. Much of it has been the same kind of work on the alteration of common rock-forming minerals.

We can, therefore, compare the present condition of the subject to the preliminary survey for a topographic map of a newly described land; several prominent points and easily accessible routes are known, which afford us some knowledge of the general configuration of the field, but few, or none of

the details. The fruits to be obtained from this land, *i.e.* knowledge concerning paragenetic relations of silicates in aqueous solutions at high temperatures, are so desirable that it will be worth while to indicate some of the salient points that have been gained, and to discuss briefly some of the dangers and uncertainties along the routes leading to other important positions in the field.

Many minerals occur again and again in hydrothermal and pneumatolytic experiments, yet very few attempts have been made to define the regions of stability for any of them in terms of temperature, pressure, composition, and pH value. There is not enough information in the literature so that one can make such a definition of the region of stability for any mineral. However, a summary of the available information does give some indication of the "conditions of formation" of a number of minerals that have been prepared numerous times by various workers.

In the following brief outline the ranges of conditions are given through which some of the minerals most commonly encountered are apparently stable. These ranges must not be taken as defining the regions of stability for any of the minerals concerned because:

(1) Metastable phases are likely to occur.

(2) Uncertainties of identification and incomplete or inaccurate statements of conditions for many of the experiments make the results unreliable quantitatively.

(3) The range of conditions covered by the experiments may not cover the entire stability range for a given mineral. In particular, it should be emphasized that the highest temperature recorded for a mineral is likely not to represent its upper limit of stability, since most of the experiments were performed at temperatures under 600° C. In cases where it seems that the upper temperature limit has been determined it is specifically so stated in the discussion. In all other cases it should be realized that the maximum temperature given is merely the highest at which the mineral has been reported

formed in the experiments, and not the highest at which it is stable.

In most of the articles abstracted the temperatures are recorded, but in many of them the compositions are given only in a general way. For this reason the following summary centers around "temperatures of formation," with remarks about the influence of concentration and other factors where they seem to be justified. It must be realized, however, that original compositions may mean very little because (1) some of the components are often added in a form in which they are relatively insoluble or unreactive under the conditions of the experiment and equilibrium may never be reached, and (2) in many runs where much of the material is crystalline secondary and tertiary phases will likely be present and at first glance will seem to be out of place.

Examples.—The various forms of silica are quite inconsistent in the temperatures at which they occur. *Cristobalite* has been reported to crystallize at temperatures ranging from 180 to 1200° C., from acidic and neutral solutions and in one instance from a solution containing *ca.* 1% NaOH. *Tridymite*, from 175–550° C. from the same types of solutions and from those in which $Na_2O:SiO_2 = 1:4$ and $1:3$. *Quartz*, from 100–750° C., also from acidic and neutral solutions with amorphous silica, silica gel, and colloidal silica, as well as from mixtures in which the alkali : silica ratio is as high as 1 : 1.

Albite is reported to have formed in one experiment at 385°±, but in all the other work it appears from 430–520°. It seems to form more readily when there is more silica present than required by the formula, analcite commonly forming when the composition of the solid components of a given run aggregates that of albite.

Orthoclase likewise forms readily from 360–520°. It has been reported from mixtures having both a higher and a lower silica ratio than that of orthoclase, even from mixtures having the composition of leucite. Orthoclase was shown by Morey and Bowen [26] to melt incongruently, but from the

[26] Morey, G. W., and Bowen, N. L.: Am. J. Sci., 5th ser., vol. 4, p. 1, 1922.

hydrothermal results it appears probable that in the temperature region mentioned above it is not decomposed by water. This indicates that with addition of water, and lower temperature, the boundary between leucite and orthoclase changes from a silica content higher than that of orthoclase to between orthoclase and leucite. This shifting of boundaries from higher to lower silica ratios as the result of the inclusion of water as a component is in harmony with the shifting of the equilibria in the system, H_2O-K_2O-SiO_2 (89) and may be a general tendency of importance. *Adularia* is reported at 300° and 245°.

Nepheline and *kaliophilite* are said to crystallize slowly at 200° and they form readily at 330–600°. Silica : alkali ratios of runs in which they have formed range up to 5 : 1, with silica reaching a maximum of nearly 70 mol. %. They form more readily, however, when the ratio is less than 1 : 1.

Zeolite formation begins at about the boiling point of water and 450° seems to be near the upper limit for most of the zeolites whose formation has been reported. Exceptions are: *analcite*, up to 550°; natrolite, up to 600°; Na thomsonite (?), up to 530°. Zeolites form, as would be expected, from solutions rich in alkali and water. Analcite has been reported from a run in which the mol. % of silica approached 70, but in general zeolites form more readily when the ratio alkali : silica approaches unity.

There are no undoubted syntheses of *biotite* and *chlorite* from their components. However, chlorite has been recrystallized, and has been formed from biotite and from augite. 400° has been suggested as the upper limit for chlorite and the lower one for biotite, but other workers report chlorite at 550° from augite and at 500–600° from muscovite.

Muscovite has been reported at temperatures from 225–450° both as synthesized from its components and as an alteration product of other minerals.

Much work has been done recently on the *clay minerals*.

Kaolinite[27] is reported by various workers from 225–400°; *dickite* is mentioned in one paper as forming in the upper part of this temperature range, at *ca.* 350°. Another worker reports *montmorillonite* from similar mixtures in the same temperature range and believes that the montmorillonite forms from solutions of higher alkalinity than kaolinite. 400° is apparently about the maximum temperature for kaolinite formation. Above that temperature *pyrophyllite* forms from mixtures that below 400° give kaolinite. Pyrophyllite has been reported from 340–550° and in one article the suggestion is made that the optimum temperature is *ca.* 470°. Later work reports pyrophyllite at 250°. *Beidellite* is reported from 350–390° under conditions that make it possible that traces of Na_2O determined its formation in preference to kaolinite or pyrophyllite.

From mixtures richer in alumina than those yielding the clay minerals *boehmite* forms from room temperature to 500° and the latter temperature may be the maximum for boehmite. *Corundum* forms from these Al_2O_3-rich mixtures above 450° and was reported at 300° in one run in which there was some NH_4F.

The difficulty of identifying the clay minerals with any degree of certainty affords an excellent example of the care that must be taken to establish the fact that a given mineral has really been synthesized. The mineral must be positively identified. There are at least four different methods of identification in general use:

[27] Current usage of the terms *kaolin* and *kaolinite* is not consistent. In the following discussion and in the bibliography the authors have sought to abide by the usage of Dana-Ford (4th ed.); *i.e.*, to use *kaolin* as a group name and *kaolinite* as the specific mineral name correlative with *nacrite* and *dickite*. Thus, in the abstracts where the mineral has been prepared and definite properties are given it is evident that the specific mineral is meant, and the term *kaolinite* is used even though the author may have called the material *kaolin* in the original paper. This does not apply to the titles, which are given *verbatim*. On the other hand, where natural material was used in experiments and no properties are given, the term *kaolin* is used, as given in the original papers, although the material used in many of these experiments may have been relatively pure *kaolinite*. Likewise, in the general discussions of the alteration of feldspar in nature the term *kaolin* is used, except where it is evident from the context that *kaolinite* is meant, as when its conditions of formation are contrasted with those of the other clay minerals.

1. *Microscopic identification* is probably the soundest method. If the crystals are large enough so that their optical properties can be determined there is no question as to their identity.

2. *X-ray analysis* must be used in the study of the clay minerals, because the crystals are always too small for microscopic identification. This method must be applied with extreme caution because

(*a*) The product studied is likely to be a mixture of two or more minerals, especially when the clay minerals are produced by alteration of other minerals and

(*b*) The patterns of the different clay minerals are so similar that it is difficult to distinguish them with any degree of certainty when they are made from separate minerals. When two or more of them are mixed positive identifications become almost impossible.

These cautions apply with equal force to other mineral groups, but are applied specifically to the clay minerals as an outstanding example because so many X-ray "identifications" of these minerals have been made of late.

3. *Chemical analysis* is nearly always meaningless unless the material can be shown under the microscope to consist practically entirely of one crystalline phase. If this can be done it will usually be much simpler to effect a microscopic identification, except for crystals that have not been previously described.

4. *Dehydration curves* for hydrous phases have almost certainly been over-interpreted in some cases. Cautions:

(*a*) There must be a *definite* break at a *definite* temperature for a given mineral. The dehydration reaction must correspond to a real reaction, reversible both in theory and in practice. The reaction requires the formation and the presence of the crystalline product or products, as well as the removal of vapor.

(*b*) As in X-ray work mixtures of two or more phases are likely to be confusing.

(*c*) Different hydrous minerals may lose water at nearly

the same temperature. For example, pyrophyllite and montmorillonite lose most of their water at 600°; kaolinite and boehmite, at 400°. Any or all of these minerals might occur in a given run of the proper composition and at the proper temperature, yet interpretations of the results of such runs have been based on dehydration curves!

Identification of the phases may be correct and the results still have little quantitative meaning if equilibrium was not attained during the run. There are two prime factors in attaining equilibrium:

1. Start with homogeneous material.
2. Allow sufficient time.

The best way to be sure of the homogeneity of the original material is to fuse it and quench it to a glass. Fusion should be repeated, with intermediate crushing, until the index of the glass is uniform throughout. The glass is then finely powdered and mixed with the desired amount of water. Coprecipitated gels may be made to approach, but never quite equal, the homogeneity of a glass.

Some idea of the time required to reach equilibrium for a given kind of run may be obtained by comparing results of runs of the same composition made with varying times. It is further necessary that the equilibrium relationships be known in the anhydrous systems before introducing water as an additional component. It was the realization of the futility of further experiments in which there was not reasonable assurance that equilibrium would be reached that caused the hydrothermal work of the Geophysical Laboratory to be stopped until the phase equilibrium relationships in the systems containing the oxides of potassium and sodium could be studied. The remark may be added that to prepare a homogeneous mixture suitable for constructive hydrothermal work is not an easy matter, and requires rigid adherence to a carefully worked out technique.

It seems altogether probable that conditions similar to those which characterize hydrothermal syntheses occurred in nature during the following processes: cooling of igneous

rocks with subsequent pegmatitic and pneumatolytic action, formation of mineral veins, origin of fumaroles and hot springs and processes of hydrothermal metamorphism. Between these natural parageneses and those produced artificially there is, on the whole, substantial agreement. It must be remarked, however, that many syntheses have been made from mixtures rich in alkali, and that the minerals of the epidote-zoisite group have never been produced artificially in presence of water. The formation of analcite, the zeolites and members of the cancrinite group from eruptive rocks rich in alkali often corresponds, at least in part, to a hydrothermal transformation. In hydrothermal and pneumatolytic vein formation the commonest minerals are quartz, albite, orthoclase, mica, chlorite, hematite, etc., namely, those which appear oftenest in the course of hydrothermal work; the fact that the members of the sodalite-nosean-cancrinite group, as well as leucite, nepheline and analcite, are rarely found is probably due to the high silica content of most natural solutions, a circumstance which is shown by the formation of quartz. The significance of hydrothermal work for metamorphic processes lies in the fact that it has been demonstrated in this way that feldspars can be formed in the presence of aqueous solutions at temperatures ranging from 300°–500°. This is important because, since many metamorphic rocks are known in which the feldspars have been altered into hydrated minerals, it gives ground for believing that the temperature at which many metamorphic processes occurred may be considerably lower than is generally supposed. All these deductions are of course merely qualitative; the quantitative study of such systems has barely begun, and is attended by such difficulties that it will, at best, be a slow process. At the same time the qualitative agreement is quite good and of considerable geologic importance.

The effect of the presence of carbon dioxide in the water is of interest in connection with the formation of veins and other types of mineral deposits. Experiments in this direction

were made by Königsberger and Müller (75, 79); their conclusions are not unexceptionable, and conflict with some of their own experimental results. In particular, their deduction with regard to the rapid increase in acidity of silicic acid with increase of temperature—while it may be true—does not, of necessity, follow from any facts yet ascertained. That the silicates are hydrolyzed, there is no doubt; but nothing definite is known with regard to the extent of this hydrolysis, even at ordinary temperature. At ordinary temperature the metasilicates are apparently almost completely hydrolyzed, the silica formed by the process separating in colloidal form; but it must be emphasized that from this fact no certain conclusion as to the strength of metasilicic acid can be drawn. Moreover, it does not necessarily follow that the salts of other silicic or aluminosilicic acids, or even metasilicates at higher temperatures, will be hydrolyzed to the same extent, especially if the silica does not separate in colloidal form. The real dissociation constant—the magnitude of which is at present altogether unknown [28]—can be determined from hydrolysis experiments only if the silica does not separate in colloidal form. From these considerations it is evident that an apparent rapid increase in the acidity of silicic acid does not necessarily imply the reality of this increase. Königsberger and Müller also ascribed the precipitation of quartz on cooling to the displacement of the hydrolytic equilibrium of carbonic acid, but from the data given such a conclusion is hardly justifiable; for of the experiments made in which carbonic acid was present, some gave considerable quartz while others gave none. The effect of the basic ion of $NaHCO_3$ seems much more significant.

The preceding brief summary has intentionally been made somewhat briefer than the data might have warranted. The few quantitative observations hitherto made have in part been discussed by their authors, but this most important side of

[28] There are reasons for supposing it to be considerably greater than it has in general been assumed to be.

the problem requires much more thorough investigation than has yet been accorded to it. It must again be emphasized that quantitative research in this field—in particular, the ascertainment of the real stability relations—is a matter of considerable difficulty, owing to the special solubility relations and to the complications consequent on the restriction of a large part of the reaction practically to the solid phase; apart altogether from the purely technical troubles associated with the high temperatures and considerable pressures involved. The knowledge of hydrothermal relationships is, however, of such importance to petrology that these difficulties will, in time, doubtless be surmounted. As a starting point for further and better investigation, and as an indication of the limitations of present knowledge of this field, the bibliography which we give will, it is hoped, prove useful.

CONCLUSION.

In this paper we have assembled all the available data relating to hydrothermal and pneumatolytic syntheses of silicates, data which unfortunately afford us practically no reliable quantitative information. Moreover, qualitatively even, the data leave much to be desired; for many minerals have been obtained but once by a given investigator, in a manner which was not reproducible and under conditions which were not specified. The minerals which have been most commonly obtained are chiefly those which are stable—or at any rate appear to be stable—over a wide range of conditions; for example, quartz and the feldspars. In all cases the crystals obtained are very small, so that accurate chemical analysis is usually out of the question; their identification even by optical or X-ray methods may be doubtful. In the preceding pages and in the annotated bibliography we have given and used the mineral names assigned by the investigator to the various products, but in doing so we accept no responsibility for their correctness; in certain cases

where the identification seemed doubtful we have placed a question mark beside the name in question.

Hydrothermal syntheses, like the paragenetic relationships investigated by van't Hoff, are determined by the solubility relations of all the possible solid phases which may be formed from the components present in the solution, although the concentration of these components in the solution is vanishingly small. Many of the reactions are, without doubt, practically restricted to the solid phase, although they take place through the medium of the solution. These solubility relationships are thus not simple; and study of the question is further complicated by the frequent appearance of metastable phases, which again is coordinated with the rates of the various possible reactions. Rates of reaction are often affected very greatly by factors which, in other respects, are of minor importance; hence slight differences—*e.g.*, in the composition, or even in the texture or fineness of grain, of the initial solid phase—may exert considerable influence on the result. These considerations enable us to see that there may in certain cases be difficulties in the way of always being able to reproduce a given result; in order to do this in any case, it is necessary to control carefully the amount of water relative to the volume of the containing vessel (the degree of filling), the temperature, and, if possible, the pressure also. The critical point of water is only a secondary factor in determining the nature of the product, its influence being effected principally through the change in concentration of the solvent (liquid or fluid) in the neighborhood of the critical point.

The thorough investigation of hydrothermal syntheses is thus beset with many difficulties, apart from the technical problems inherent in operating on heterogeneous systems within closed bombs at high temperatures. Nevertheless, our knowledge of the real relationships of these minerals can be advanced materially if care is taken to control the factors involved, the most important of which are the initial compo-

sition of the system (including therein the relation between the amount of water and the volume of the bomb) and the temperature.

THE BIBLIOGRAPHY.

The papers are arranged in chronological order. In the index at the end of the bibliography distinction is made between minerals used in the experiments and those produced by them. Oxides, carbonates, and other minerals have been included in the index where they are mentioned in papers dealing with silicates, and a very few papers dealing entirely with minerals other than silicates are included in the earlier abstracts. In the bibliography itself the mineral names in boldface type are those of minerals formed in the experiments; the italicized ones, those of minerals used as original materials.

We have attempted no systematic discussion of the hydrothermal and pneumatolytic alteration of minerals, because there has been no systematic experimental study. We have merely recorded and indexed the alterations as found in the literature.

Since many of these experiments were performed at temperatures greater than the critical temperatures of the solutions, some of the minerals must have been formed from a gaseous phase. Some of these experiments have given rise to the very interesting problem of the transport of non-volatile material, especially silica, by water in the supercritical state.[29] Papers relating to the "volatile transfer" of silica are included in the bibliography even though some of them do not record the formation of minerals. They are listed in the index under "Quartz, solubility and transport of silica."

A few papers are included which are merely general discussions, summaries, and descriptions of apparatus. These papers are not indexed, except that their authors are included in the complete author index.

[29] See Ingerson, E.: Relation of critical and supercritical phenomena to geologic processes. ECON. GEOL., vol. 29, pp. 454–470, 1934, for an outline of the geologic implications of this problem and a summary of additional pertinent experimental work.

1845 1
1848 2
1851 3
1855 4
1857 5

1845 SCHAFHAUTLE: *Münchener gelehrte Anzeigen*, 1845, p. 575. (Cited by L. Bourgeois, *Reproduction artificielle des minérals*, Paris, **1884,** p. 80.) Prepared **quartz** by heating gel SiO_2 with H_2O in an autoclave.

1848 WÖHLER: Cited by Bunsen. *Ann.*, **65**, 80. **Apophyllite** heated with H_2O at 180°–190° under a pressure of 10–12 atm. was recrystallized.

1851 SÉNARMONT, H. DE: Sur la formation des mineraux par voie humide . . ., *Ann. chim. phys.*, [3] **32**, 142–5. Used glass tubes, generally enclosed in steel tubes, SiO_2 gel, and H_2O containing HCl or CO_2, heated at 200°–300°; product **quartz** in six-sided striated prisms with pyramidal terminations. When the solution contained $NaHCO_3$, CO_2 and some realgar, very little **quartz** was obtained.

1855 MASCHKE, O.: Vorläufige Mittheilungen über Kieselsäurehydrat und die Bildungsweise des Opals und Quarzes, *Z. deut. geol. Ges.*, **7**, 438–42. In previous experiments (*Erdmann and Werther's J. prakt. Chem.*, **61**, Heft 1) in which solutions were heated on the water bath in closed glass tubes, hard pyramidal **quartz** crystals were obtained, insoluble in acids and alkalies. In this paper are described experiments in which evaporation of solutions containing SiO_2 gave **opal,** both at room temperature and on gentle heating.

1857 DAUBRÉE: Observations sur le metamorphisme et recherches expérimentales sur quelques—uns des agents qui ont pu le produire, *Ann. Mines*, [5] **12**, 289–326. Substances were heated with H_2O in a glass tube, which was placed in a steel tube, and the space between filled with H_2O. *Glass* with but little H_2O at 400° gave a white, porous mass containing **quartz** and **wollastonite** (?). The solution contained SiO_2, 37%; Na_2O, 63%; K_2O, trace; corresponding approximately to $3Na_2O \cdot 2SiO_2$. Feldspar contained in an obsidian was not noticeably attacked. *Pyroxene* or *muscovite*, heated alone with water, was unchanged except for a coating of **quartz.** When the water from the hot springs at Plombiéres, which contains much potassium silicate, was heated for 2 days, much **quartz** was deposited, most of which was stated to have come from the alkali silicate. *Kaolin*, treated with the Plombiéres water, gave crystals of **feldspar** with a little **quartz.** When the same water was concentrated and heated in a glass tube, the latter was attacked, giving in part greenish crystals, having a prism angle like **augite.** Composition: SiO_2, 51%; CaO, 26%; FeO, 22%; MgO, trace. Similarly treated, wood gave a mass resembling **anthracite.** Daubrée, in his *Synthétiques de Géologie Expérimentale*, Paris, **1879,** pp. 154–179, describes the same experiments, with crystallographic figures of the minerals obtained. He also

speaks of a third mineral found in the white decomposed mass of the glass tube, having the composition of **pectolite;** and a fourth mineral which he called **chalcedony.** No crystallographic details are given.

1861 6 DEVILLE, ST. CLAIRE: Etudes analytiques sur les matieres alumineuses, *Ann. chim. phys.*, [3] **61**, 309–42. Evaporation experiments with *bauxite* and NaOH. The results were not very definite, but the product contained, among other things, **corundum.**

1862 7 DEVILLE, ST. CLAIRE: Reproduction de la Lévyne, *Compt. rend.*, **54**, 324–7. Solutions of K silicate and Na aluminate in glass tubes at 170° gave hexagonal tablets of **levynite,** optically uniaxial, composition: SiO_2, 44.7%; Al_2O_3, 21.5%; CaO, 0.9%; Na_2O, 5.5%; K_2O, 8.6%; H_2O, 19.7%. The solution remaining contained neither Al_2O_3 nor SiO_2 in noticeable amounts. A similar mixture at higher temperature gave little **levynite,** but much **quartz** (?), and the solution contained Na and K aluminates. Mixtures of K silicate and K aluminate at 200° gave **K ittnerite** (**nosean**), composition: SiO_2, 34.1%; Al_2O_3, 28.9%; K_2O, 24.8%; H_2O, 11.5%. A mixture of K silicate and Ba aluminate gave, under similar conditions, a **crystalline product,** composition: SiO_2, 35.3%; Al_2O_3, 10.2%; BaO, 30.0%; K_2O, 5.8%; H_2O, 18.9%.

1872 8 MASCHKE, O.: Ueber Abscheidung krystallisirter Kieselsäure aus wässrigen Lösungen, *Ann. Physik Chem.* (*Poggendorf*), [5] **25**, 549–78. Using an aqueous solution of $Na_2O.4SiO_2$ in a sealed glass tube at 175–185°, obtained an alkaline solution and a fine-grained precipitate containing (1) needles of a **crystalline hydrated silica,** (2) aggregates of **hydrated silica.** (**Opal**?) On the walls of the glass tube were concretions, the nuclei of which were **crystalline anhydrous silica,** the outside a **crystalline hydrated silica** different from the above. The nuclei were stated to contain both **tridymite** and **quartz;** at 175–185° more **tridymite;** at 195–205° more **quartz.** Maschke states that these concretions were formed during cooling.

1873 9 CHROUSTSCHOFF [Kroustchoff, K. de], K. VON: On silicic acid and the silicification of woods, *Am. Chemist*, **3**, 281–6. Used a dialyzed colloidal solution of silica, heated at 250° in a glass tube for 14 days, and obtained a crystalline powder; density, 2.66–2.80, in small hexagonal prisms, probably **tridymite.** At 350° for 14 days in a gold-lined steel tube, using the same colloidal solution, hexagonal plates, probably of **tridymite,** were formed; density, 2.25–2.51.

1876 10 LEMBERG, J.: Ueber Silicatumwandlungen, *Zeit. deut. geol. Ges.*, **28**, 519–621. Many experiments were made with *kaolin* and *zeolites* in aqueous salt solutions at 100° and at 180–195° to study the replacements of the alkali of the *zeolites* by that of the salt

used, and the transformation of the *kaolin*. Most of the products were amorphous. *Leucite* in 18 hours at 180–190° with NaCl solution gave a product of the composition of **analcite,** which, when treated with K_2CO_3 solution, regenerated **leucite.** The replacement was more difficult when the *leucite* had first been ignited. The Mg of $MgCl_2$ and the Ca of $CaCl_2$ replaced K or Na only partially at 100°; *nepheline* was more resistant to replacement. *Kaolin* and $Al(OH)_3$ with alkaline silicate solutions at 100° and 180° gave amorphous "compounds." From many experiments with *zeolites* and salt solutions below 200° Lemberg concluded that **natrolite, scolecite,** and **mesolite** can each be transformed into the other in this manner.

1879 11 FRIEDEL, CHARLES, AND SARASIN, EDMOND: Reproduction artificielle du quartz cristallisé, *Bull. soc. min.*, **2**, 113–17. Two experiments were made, in which a mixture of KOH, precipitated $Al(OH)_3$, and a large excess of silica gel were heated with water at a temperature below dark red heat. The first experiment, heated for 18 hours, gave hexagonal crystals of **quartz,** with parallel extinction, and faces $(10\bar{1}0)$, $(10\bar{1}1)$, $(01\bar{1}1)$. The second experiment, heated for 38 hours, gave much larger crystals (0.5 mm. long and 0.1 mm. broad); six prism angles could be measured on the goniometer. Prisms hexagonal, striations horizontal, unequally developed $(10\bar{1}1)$ and $(01\bar{1}1)$; some crystals showed sharp rhombohedra, $(10\bar{1}1)$, also with rarer faces. Photomicrographs are given.

1879 12 FRIEDEL, C., AND SARASIN, E.: Sur la production d'une matière feldspathique, *Bull. soc. min.*, **2**, 158–61. Experiments were made at temperatures below dark red, the heating being continued for 36 hours. Using K silicate, a small amount of KOH, and a precipitate obtained by adding $AlCl_3$ to K silicate, obtained a product considered to be a mixture of **orthoclase** and **quartz.** (It is stated in this paper that **orthoclase** was obtained in the previous experiment.) **Orthoclase,** determinable faces perpendicular to the plane of symmetry (010), outline imperfectly hexagonal, or a parallelogram, birefringent, small, angle corresponding to $(\bar{1}01) \wedge (100) = 140°$ (probably typographical error, for orthoclase should be 114°). Faces present, (010), (100), $(\bar{1}01)$. An analysis of the product is given; the results do not correspond to orthoclase, but as the sample analyzed was contaminated to an unknown degree, the analysis is meaningless. Density, determined with Thoulet's solution, sensibly that of orthoclase. **Quartz** was obtained in the ordinary forms; when the temperature was higher hexagonal crystals of **tridymite** were found.

1880 13 FRIEDEL, C., AND SARASIN, E.: Sur un silicate artificiel resemblant à l'orthose, *Bull. soc. min.*, **3**, 25–6. Using a mixture of precipi-

tated K-Al silicate, K silicate and H_2O, under conditions similar to those in the preceding experiments, obtained **orthoclase** and **quartz,** the former with crystal faces parallelograms, extinction with the larger dimension = 3–4°, terminal faces formed angle corresponding to (001) ∧ ($\bar{2}$01) of **orthoclase;** (110) missing. **Quartz** in short bipyramids without prism faces.

1880 **14** MEUNIER, STAN.: Production et cristallisation d'un silicate anhydre (enstatite) en présence de la vapeur d'eau à la pression ordinaire, *Compt. rend.*, **90**, 349–51. Mg was placed in a porcelain tube, one end of which was connected to a source of steam, the other with a source of $SiCl_4$ vapor. When both gases were passed over the Mg at a low red heat, at atmospheric pressure, the reaction was $Mg + SiCl_4 + 3H_2O = MgO \cdot 2SiO_2 + 4HCl + H_2$. The crystals obtained were called by Meunier **enstatite,** but Fouqué and Lèvy, *Synthèse des Mineraux et des Roches*, Paris, **1882,** p. 111, showed that it was a **monoclinic Mg pyroxene.**

1880 **15** MEUNIER, STAN.: Reproduction artificielle du spinelle et du corindon, *Compt. rend.*, **90**, 701–2. H_2O vapor was passed over $AlCl_3$ and Mg contained in an open tube, heated to a low red heat. The product was mainly **spinel,** in hard colorless isotropic cubes and octahedra, not altered by boiling HNO_3. In other parts of the tubes were crystals of **periclase** and **corundum.** No crystallographic details are given.

1880 **16** MEUNIER, STAN.: Reproduction synthétique des silicates alumineux et des silico-aluminates alcalins de la nature, *Compt. rend.*, **90**, 1009–12. Experimental conditions the same as in (14), but Al was used instead of Mg. When the $SiCl_4$ was in excess, lamellae and needles of metallic **silicon** were obtained; when the water was in excess, amorphous " compounds " containing Si and Al; and when both vapors were present in equal amounts, small needles of the composition $\mathbf{Al_2SiO_5}$ (SiO_2, 40.91%; Al_2O_3, 58.02%) were obtained. These crystals were slightly birefringent. When KOH was added to the charge, brown, isometric, completely isotropic trapezohedra of **leucite** were obtained; size 0.003–0.012 mm. Composition: SiO_2, 55.83%; Al_2O_3, 23.54%; K_2O (by difference), 20.63%. At a slightly different temperature prisms showing **orthoclase** twinning were obtained but in quantities too small for analysis.

1880 **17** SCHULTEN, A. DE: Sur la reproduction artificielle de l'Analcime, *Bul. soc. min.*, **3**, 150–3; *Compt. rend.*, **90**, 1493–5. Heated sodium silicate solution, sodium hydroxide and an aluminous *glass* for 18 hours at 180–190°. The product was **analcite** in crystals 0.1 mm. long, imbedded in gelatinous silica. The crystals were separated from the impurities by successive treatments with NaOH and

dilute hydrochloric acid, though the crystals were somewhat soluble in the latter. An analysis of the product so treated gave: SiO_2, 54.6%; Al_2O_3, 21.8%; Na_2O (by difference), 15.0%; CaO, trace; H_2O, 8.6%. The crystals were isometric trapezohedra (211), optically abnormal like the natural mineral; apparently a complex twin composed of 4 pyramidal individuals, with base on the supposed octahedral faces, and apexes meeting in the center. Individual crystals optically uniaxial and positive, ω on the supposed octahedral face, ϵ perpendicular to this face.

1881 **18** FRIEDEL, C., AND SARASIN, E.: Sur la reproduction par voie humide de l'orthose, *Bull. soc. min.*, **4**, 171–5. **Orthoclase** and **quartz** were obtained by heating a mixture similar to that used in (13), but containing more $Al(OH)_3$. Analysis of the product gave: SiO_2 (by difference), 70.03%; Al_2O_3, 15.59%; K_2O, 14.38%. This composition corresponds to **orthoclase,** plus about 5.4% **quartz.** The **orthoclase** showed the following forms: (1) Like **orthoclase** in granite, with (010) prominent and bounded by (100) or (110) and (001), and ($\bar{2}01$) or ($\bar{1}01$). Extinction on (010) against trace of (100) = 22°, and against the trace of (001) = 4–5°; (2) **orthoclase** as in trachyte, with faces (001) and (010) dominating and (110) subordinate; (3) **adular orthoclase,** with (110), (001), and sometimes ($\bar{1}01$). Angles (measured microscopically); (001) ∧ (100) = 116–117°; (001) ∧ ($\bar{1}01$) = 129–130°. Angle on base about 113°; on (110), 104°. Twinning parallel to (001), extinction against (001), 7–8°. Also Baveno twinning. In some of the experiments, in which there was much K silicate, a **hydrated K silicate** was obtained in crystals 2 to 3 mm. in length. These crystals were slightly attacked by HCl, fusible at pale white heat with intumescence; orthorhombic, with (010) prominent and supplemented by (001) and (110). Prism angle = 105° 8′, axial plane parallel to (010), acute bisectrix perpendicular to (100); $\rho > v$.

1881 **19** FRIEDEL, C., AND SARASIN, E.: Sur la reproduction par voie aqueuse du feldspath orthose, *Compt. rend.*, **92**, 1374–8. Used a steel bomb 1 cm. thick, lined with copper and platinum at a temperature near dull red heat. Data the same as in (12), (13), and (18).

1882 **20** SCHULTEN, A. DE: Sur la reproduction de l'analcime, *Bull. soc. min.*, **5**, 7–9. With less detail in *Compt. rend.*, **94**, 96–7. Obtained **analcite** by heating for 18 hours at 180° C. in a copper bomb a mixture of sodium silicate and sodium aluminate in such proportions that the $Al_2O_3 : SiO_2$ ratio was the same as in analcite, together with a " convenient quantity " of lime water. The latter was merely to aid crystallization, since without it good crystals were rarely obtained. The crystals were similar to those obtained in

(17); trapezohedra and cubes that were mostly isotropic. However, some optically abnormal crystals were found in the product of one of the experiments. Schulten believed that the trapezohedra were formed from very concentrated and alkaline solutions, the cubes under other conditions.

1882 21 SCHULTEN, A. DE: Sur la reproduction artificielle d'un silicate hydraté cristallisé, *Compt. rend.*, **94**, 992–3. A mixture of K silicate and $Ca(OH)_2$ solutions was heated to 180° in a glass tube. The product was crystals that fused with intumescence and were slowly decomposed by HCl. Parallel extinction, high birefringence, positive elongation. Composition: SiO_2, 64.2%; Al_2O_3, 0.7%; CaO, 14.7%; Na_2O, 3.3%; K_2O, 2.2%; H_2O, 14.5%; corresponding to $(K_2Na_2Ca)O \cdot 3SiO_2 \cdot 2H_2O$.

1882 22 RAMSAY, W., HUNTER, AND OTHERS: Report of a committee in *Rept. Brit. Assn.*, **1882**, 239–40. Used a cast iron bomb, which remained tight at 300–400°. Water had no effect on finely powdered *quartz* at 300°. Powdered *chalcedony* similarly treated was but little attacked; amorphous silica was caked into a hard, white, opaque glassy mass.

1883 23 FRIEDEL, C., AND SARASIN, E.: Sur la reproduction de l'albite par voie aqueuse, *Compt. rend.*, **97**, 290–4. When SiO_2, NaOH solution, and Al_2O_3 in the proportions of albite were heated at 400° in a steel bomb no albite was formed, but **analcite,** in trapezohedra that showed no birefringence. There were also **globulites** and undeterminable **needles.** When sodium silicate corresponding to the amount found in the solution in the preceding experiment was added to the same mixture as before and heated to 505°, 517°, or 432°, the product was needles or tablets of **albite,** flattened parallel to (010), 0.1–0.2 mm. long and half as broad and with most of the crystals elongated parallel to the intersection between (001) and (010). These crystals have an extinction against the elongation of 15–19°. Some are elongate parallel to the intersection of $(1\bar{1}0)$ and (110) and have an extinction angle of 4°. $(1\bar{1}0) \wedge (010) = 116–118°$. Re-entrant angles indicated albite twinning; extinction = 16–17° between adjacent lamellae. Composition: SiO_2, 68.93%; Al_2O_3, 19.23%; Na_2O, 11.61%. Quartz was never found.

When KCl in increasing amounts was added to the charge without changing the alkalinity at *ca.* 500°, first **quartz** and **unknown cubic crystals** were obtained, then large **albite** crystals, together with small undeterminable crystals similar to **orthoclase.** Analysis of the small crystals mixed with some **albite** gave: Al_2O_3, 18.89%; Na_2O, 8.53%; K_2O, 3.94%, corresponding to about one-half orthoclase. The crystals seemed to be of two kinds. **Albite**

was still obtained when the K_2O : Na_2O ratio was 4 : 1. The presence of NaCl did not affect the crystallization.

1883 **24** GORGEU, ALEX.: Sur la production artificielle de la rhodonite et de la tephroite, *Compt. rend.*, **97**, 320–3. H_2 or CO_2 saturated with water was passed over a mixture of 1 part precipitated silica and 10 parts $MnCl_2$ at red heat. The product varied with the time of heating. The first product obtained was red crystals of **rhodonite,** $MnO \cdot SiO_2$, which on longer heating were transformed into gray crystals of **tephroite,** $2MnO \cdot SiO_2$. Gorgeu states that the H_2 and CO_2 only served to prevent oxidation, but were themselves without action. Large amounts of alkali chlorides hindered the process, but the result was the same. In the presence of $CaCl_2$, $MgCl_2$ and $FeCl_2$ the product had the general composition: $\mathbf{2RO \cdot SiO_2}$, the RO being 1% CaO, 3% FeO, 9% MgO. The silicate prepared in the presence of $ZnCl_2$ never contained Zn. The **rhodonite** had a glassy luster, density 3.68, triclinic prisms; the **tephroite** had an adamantine luster, density 4.08, orthorhombic prisms. The salts were hardly oxidized in dry air, difficultly fusible at red heat, and could be recrystallized from molten $MnCl_2$. *Rhodonite* dissolved in molten $MnCl_2$ in the presence of H_2O vapor gave **tephroite;** *tephroite* with SiO_2 in $MnCl_2$ gave **rhodonite** when protected from the action of air and H_2O. (M.p. of $MnCl_2$ = 650° C.)

1883 **25** GORGEU, ALEX.: Sur la production artificielle de la spessartine artificielle ou grenat manganésifère, *Compt. rend.*, **97**, 1303–5. H_2 and steam were passed over a mixture of 20–25 g. $MnCl_2$ and 1.5 g. pipe clay in a Pt crucible at cherry red heat for ½ hour; product a reddish fused cake containing $MnCl_2$ and **spessartite,** the latter in yellowish trapezohedra, 0.03–0.5 mm. long, insoluble in HCl, fusible at a strong red heat, $d_{11}° = 4.05$, hardness = 6–7, composition: SiO_2, 36.10%; Al_2O_3, 21.25%; MnO, 42.70%; CaO, MgO, trace. When $CaCl_2$ was used, crystals were obtained which possibly were **grossularite.**

1883 **26** LEMBERG, J.: Zur Kenntniss der Bildung und Umwandlung von Silicaten, *Z. deut. geol. Ges.*, **35**, 557–618. The influence of H_2O on *glasses* at 100° was studied by heating in open Pt or Ag tubes, covered with layer of paraffin to prevent evaporation; the heating was continued 10 hours every day at the same temperature. A *basalt* heated for 6 months with distilled H_2O took up 2.43% H_2O, which was not removed over H_2SO_4 in 2 weeks; the solution remaining in the tube had a slightly alkaline reaction. The same *basalt* heated with K_2CO_3 solution for 9 months gave a glass rich in H_2O, and $\mathbf{CaCO_3}$ crystals. A *glass* made from *palagonite* from Vidoe heated for 3 months with distilled H_2O at 100° was but little attacked, but the product contained 8.61% H_2O. The same *glass*

heated with Na_2CO_3 solution for 2 months gave a very strongly hydrated glass and **calcite** crystals.

A contact sintered *sandstone* heated with Na_2CO_3 solution gave a glass containing much H_2O, and considerable SiO_2 went into solution. When a *glass* obtained by heating *nepheline* was heated with K_2CO_3 solution all the Na was replaced by K, and the glass contained 10.89% H_2O. The ignited H_2O-rich glass gave off considerable heat when moistened, and took up 9.8% H_2O. Melted *labradorite* heated for 13 months at 100° with K_2CO_3 solution gave a glass rich in K and the Ca replaced had formed **$CaCO_3$.**

Melted *adularia* and *orthoclase* heated with Na_2CO_3 solution at 100° gave a strongly hydrated glass containing Na, and much SiO_2 went into solution. Similarly treated, *albite* glass took up H_2O, and when K_2CO_3 was used the Na of the mineral was replaced. *Augite* with K_2CO_3 solution for 1 year at 100° gave **$CaCO_3$,** the MgO remained combined with the SiO_2. Concluded that Na compounds take up more H_2O than K compounds, but when the *glasses* are ignited the K glasses take up much H_2O and show a large heat effect, while the Na glasses do not show the latter effects to the same extent. Experiments were made to study the replacements and transformations between solutions and various silicates, working with a copper digester heated 10 hours daily for the given time. *1884* **27**

Kaolin with an 8% $Na_2O \cdot 4SiO_2$ solution at 180–190° for 33 hours gave an amorphous H_2O-rich powder similar in composition to **natrolite.** (Lemberg (40) corrects this, stating that it was a **basic analcite.**) *Allophane* at 100° with water glass solution for 14 days gave an amorphous powder rich in alkali and H_2O. *Kaolin* with 30% NaOH solution for 72 hours at 180–190° gave an amorphous silicate rich in Na_2O and H_2O.

Orthoclase for 6½ months at 100° with 10% NaOH and Na_2SO_4 solution gave a product 95% crystallized in small **columns,** composition: SiO_2, 34.74%; Al_2O_3, 30.04%; CaO, 0.20%; Na_2O, 18.53%; Na_2SO_4, 9.33%; H_2O, 5.88%. *Sanidine* containing a small amount of BaO had all the Ba eliminated as $BaSO_4$ when similarly treated. *1884* **28**
Natrolite heated for 3 months at 100° with 20% NaOH and Na_2SO_4 gave **needles** of the composition: SiO_2, 34.03%; Al_2O_3, 30.24%; Na_2O, 17.75%; Na_2SO_4, 13.32%; H_2O, 5.02%. *Albite* treated 14 days at 100° with 30% NaOH gave a product 80% of which was crystalline, composed of **needles** of the composition: SiO_2, 35.14%; Al_2O_3, 29.66%; Na_2O, 17.39%; Na_2SO_4, 12.63%; H_2O, 4.90%. Similar needles were obtained with *labradorite;* these needles all had the composition of a **hydrated nosean.**

Similar experiments with K_2SO_4 and K_2CrO_4 gave amorphous products. Many other experiments were made with solutions of NaOH and KOH and different salts and the products analyzed. All experiments showed that alkalies are easily replaced, and that NaCl, KCl, Na_2CO_3, $NaNO_3$, Na_2S, and Na_2SO_4 are easily added. When solutions of Na_2SiO_3 and salts were heated with $Al(OH)_3$, minerals were obtained resembling those of the **cancrinite group; analcite** was sometimes obtained; when other salts than Na_2SiO_3 were not added **alkaline aluminosilicates,** often of simple types, were obtained.

When *anorthite,* with a little *augite,* was heated for 180 hours at 180–190° with Na_2CO_3 solution the product consisted of **calcite** crystals, amorphous substances, and a columnar mineral similar to **cancrinite.** Mixtures of $Al(OH)_3$, $CaCl_2$ and Na_2SiO_3 solution gave a mineral crystallized in bundles and sheaves, which Lemberg considered to be **pectolite.** Similar minerals were obtained by heating *wollastonite, apophyllite, okenite, datolite,* and artificial $CaSiO_3$ with Na_2SiO_3 solutions. **K pectolite** was much harder to prepare.

1884 **27** GORGEU, ALEX: Sur la production artificielle de la fayalite, *Compt. rend.*, **98**, 920–2. Heated 20 grams of previously dried and fused $FeCl_2$ and 1 gram SiO_2 at a red heat in stream of H_2 and steam, in an open platinum crucible; product a cake containing excess chloride and crystals of **fayalite,** 0.5–1.0 mm., composition: SiO_2, 28.8%; FeO, 71.2%. The product was brown, weakly magnetic, optical properties (determined by E. Bertrand) gave an acute negative bisectrix. Density 4.23, hardness = 5–5.5. $FeSiO_3$ was never obtained. When Al_2O_3 was used instead of SiO_2, octahedra of **spinel** were obtained. When MnO was present, a mineral similar to olivine was obtained, composition: SiO_2, 32%; FeO, 34%; MnO, 34%; probably **knebelite.** When 50–66% $MnCl_2$ was present, the crystals contained only 19–20% of the total basic oxides as FeO.

1884 **28** GORGEU, ALEX.: Sur l'oxychlorure de calcium et les silicates de chaux simples et chlorures, *Compt. rend.*, **99**, 256–9. When moist air was passed over melted $CaCl_2$ at red heat in an open vessel, **Ca oxychloride,** $CaCl_2 \cdot CaO$ was formed. When precipitated SiO_2 was added, with 1 equivalent of $CaCl_2$, **$CaO \cdot SiO_2$** was obtained; with 2 equivalents, **$2CaO \cdot SiO_2$;** and with 7 equivalents of chloride a **chlorosilicate** was obtained. When a mixture of 1 gram SiO_2, 15 grams $CaCl_2$, and 3 grams NaCl was heated at a cherry red, in a current of moist air, a mixture of excess chlorides, the **chlorosilicate,** round grains of **tridymite** (?), and long prisms of **wollastonite** were obtained. Details of the optical examination are not

given, but properties are stated to coincide with those of the natural mineral.

1884 29 GORGEU, ALEX.: Sur une pseudomorphose artificielle de la silice, *Compt. rend.*, **98**, 1281–2. Mentions the preparation of **fayalite** (27). By heating *fayalite* in air oxidation took place; on treating with HCl, SiO_2 pseudomorphs of fayalite remained. Experiments with artificial *knebelite* gave similar results.

1885 30 GORGEU, ALEX.: Sur plusieurs productions de mineraux naturels obtenus à l'aide des chlorures métalliques, *Ann. chim. phys.*, [6] **4**, 515–61. A collected account of the work recorded in (24), (25), (27), (28), (29), and the following additional experiments: Heated 20 grams $MnCl_2$, 1 gram SiO_2 at a red heat at atmospheric pressure in an atmosphere of H_2 and H_2O; product a **manganese chlorosilicate,** $2MnO \cdot SiO_2 \cdot 2MnCl_2$, in isometric red crystals. Using $FeCl_2$, in 2 experiments only, an isotropic **iron chlorosilicate** was prepared. Experiments on the preparation of alkaline earth and lead sulfates are also given.

1885 31 LEMBERG, J.: Zur Kenntniss der Bildung und Umbildung von Silicaten, *Z. deut. geol. Ges.*, **37**, 959–1010. About 30 grams of $Na_2SiO_3 \cdot 8H_2O$ crystals were melted in their crystal H_2O, to the melt was added 2–3 grams of *datolite*, *wollastonite*, *gypsum*, or $CaCO_3$, and the mixture heated at 190–200° for 78–100 hours. Product in each case, besides indeterminate grains, was bundles or sheaves of a **pectolite-**like mineral.

Kaolin heated for 78 hours at 195–205° with 37% KOH gave an amorphous substance of the composition: $\mathbf{K_2O \cdot Al_2O_3 \cdot 2SiO_2}$, which, when added to molten Na_2SiO_3 and treated the same as before, gave an amorphous mass. Poorly formed crystals were obtained by treating *kaolin* with 56% NaOH solution.

Nepheline with 56% NaOH gave isometric crystals. *Nepheline*, *anorthite*, *haüynite*, *sodalite*, and *ittnerite* (*nosean*) with very strong KOH or potassium salt solutions gave amorphous or poorly formed birefringent columns of composition: $\mathbf{K_2O \cdot Al_2O_3 \cdot 2SiO_2}$; KCl gave a different result. While ordinary *analcite* with K_2CO_3 or KCl solution at 100° was converted to leucite, *fused analcite* gave a **silicate** rich in H_2O.

Adularia, *sanidine* and *albite* treated with Na_2SiO_3 solution at 200° gave isometric (?) crystals, and others similar to **pectolite.** *Chabazite* could be transformed into **analcite.** *Spodumene* similarly treated with Na_2CO_3 solution showed alteration. Many other similar experiments were made, and also many replacement experiments, in which the product was usually amorphous. From many experiments it was found that sodium or potassium silicates by heating at 200° with sodium salt solutions gave compounds with

a H_2O content between 8–9%, this reaction going easier in alkaline than in acid solutions.

1885 **32** FRIEDEL, C., AND SARASIN, E.: Cristallisation de la calcite en présence d'une solution de chlorure de calcium, *Bull. soc. min.*, **8**, 304–5. Small **calcite** crystals were obtained by heating $CaCl_2$, precipitated $CaCO_3$, and 60–70 cc. H_2O for 10 hours at 500°; with 20 grams $CaCl_2$ and a few grams $CaCO_3$ the crystals were large enough for goniometric measurement. Crystals were simple rhombohedra, normal angle (goniometer) = 74°54′, − 55′, − 52′. Growth similar to crystal skeleton. No aragonite.

1886 **33** DOELTER, C.: Synthetische Studien, *Neues Jahrb. Min. Geol.*, **1886**, I, 124. Steam was passed over fused $CaCl_2$ at atmospheric pressure, temperature not stated; product rectangular **tablets,** with parallel extinction, biaxial, cleavage parallel to one direction of the rectangle, slightly soluble in cold dilute HCl, soluble in hot concentrated HCl, low hardness.

1887 **34** CHROUSTSCHOFF, K. VON: Nouvelles synthèses du quartz et de la tridymite, *Bull. soc. min.*, **10**, 31–6; *Neues Jahrb. Min. Geol.*, **1887**, I, 205–8. **Quartz** was obtained by heating a colloidal solution of SiO_2 to 250° "almost every day for 6 months." Started with 4 tubes, 3 of which burst soon, the other in 6 months. Some crystals as large as 8 mm. long and 3 wide, of type of **vein quartz,** with $(10\bar{1}0)$, $(10\bar{1}1)$, $(01\bar{1}1)$ and twice $(11\bar{2}1)$, and $(51\bar{6}1)$, striated parallel to intersection $(10\bar{1}0)$, $(51\bar{6}1)$; $(11\bar{2}1)$ also present. **Tridymite** was also formed in fusion experiments.

1887 **35** CHROUSTSCHOFF, K. VON: Notice sur une nouvelle disposition d'un appareil pour les synthèses hydrothermiques, *Bull. soc. min.*, **10**, 137–40. Description of a new form of apparatus which was used for heating glass containers up to 500°.

1887 **36** CHROUSTSCHOFF, K. VON: Sur de nouveaux procédés de reproduction artificielle de la silice cristallisée et de l'orthose, *Compt. rend.*, **104**, 602–3. Used a glass tube, heated at 250–300°, and a 10% colloidal solution of SiO_2; product **quartz,** with prism $(10\bar{1}0)$ and rhombohedron predominating, rhombohedron $(01\bar{1}1)$ little developed, $(51\bar{6}1)$ rare. Also heated at 300° SiO_2 solution, dialyzed colloidal Al_2O_3 solution and KOH; product small **quartz** crystals and rhomboidal lamellae corresponding to the **adular orthoclase** of Friedel and Sarasin.

1887 **36a** COLLINS, J. H.: On the Nature and Origin of Clays, *Mineralog. Mag.*, **7**, 205–14, 1886–87, esp. pp. 212–13.

First treated *orthoclase* and *granite* in lead tubes at high temperatures with HF vapor. The feldspar was rapidly changed to **hydrous aluminum silicate,** soluble potassium fluoride, and **silica,** which was deposited on the sides of the tube.

In later experiments dilute HF was used at 60° F. in the alteration of various feldspars. *Orthoclase* was much more readily and completely altered than either *oligoclase* or *albite*. *Labradorite* was altered only in spots, and *obsidian* was very slightly altered. Analyses are given of (*a*) an original orthoclase used in an experiment, (*b*) the inner layer after alteration, and (*c*) the outer layer after alteration. The sample was treated with dilute HF for 96 hours at 60° F.

The product was examined microscopically and "exactly resembled ordinary well-prepared (natural) kaolin"; from the microscopic evidence alone the material is taken to be **kaolinite.** There were also a number of small colorless cubes formed, which were probably **fluorite.**

1887 **37** GORGEU, ALEX.: Silicates doubles d'Alumine et de Potasse ou de Soude, *Bull. soc. min.*, **10**, 278–84, in more detail in *Ann. chim. phys.*, [6] **10**, 145–69. By acting on *kaolin* mixed with 10 parts of NaCl at red heat in the presence of H_2O vapor or HCl, an amorphous silicate insoluble in H_2O was obtained, composition: SiO_2, 41.20%; Al_2O_3, 35.70%; Na_2O, 20.40%; CaO, 0.55%; MgO, 0.65%; NaCl, 1.50%; corresponding to $\mathbf{Na_2O \cdot Al_2O_3 \cdot 2SiO_2}$ + chloride. With 20 parts KI, KBr or KCl, a crystalline compound attacked by H_2O, composition: $\mathbf{K_2O \cdot Al_2O_3 \cdot 2SiO_2}$ + halide, was produced. With K_2CO_3 and *kaolin* at cherry red heat an amorphous compound, composition: $\mathbf{K_2O \cdot Al_2O_3 \cdot 2SiO_2}$, was produced, and a similar result was obtained with Na_2CO_3, the product in this case being birefringent. At a strong, red heat octahedral crystals of the composition $\mathbf{K_2O \cdot Al_2O_3 : SiO_2}$ were obtained, together with other compounds of unknown composition. Analyses are given in the second reference; no crystallographic details.

1887 **38** FRIEDEL, C., AND SARASIN, E. *Bull. soc. min.*, **10**, 169. An announcement that the authors had prepared **topaz** by the action of H_2SiF_6 solution on a mixture of SiO_2 and Al_2O_3 at 500°. No details.

1887 **39** GORGEU, ALEX.: Production artificielle de la Wollastonite, *Bull. soc. min.*, **10**, 271–8. Worked at a red heat and ordinary pressure, passing air and steam over an intimate mixture of SiO_2 and $CaCl_2$; product obtained varied with the length of heating and the composition of the mixture. With 1 gram SiO_2 and 15–20 grams $CaCl_2$, besides calcium metasilicate, **wollastonite,** a deliquescent **calcium chlorosilicate,** $2CaO \cdot SiO_2 \cdot CaCl_2$, orthorhombic, high birefringence, axial angle about 25°; and the **calcium chlorosilicate,** $CaO \cdot SiO_2 \cdot CaCl_2$, hexagonal, optically positive, were obtained. (Gorgeu gives the formulae $2CaO \cdot SiO_2 \cdot CaCl$ and $CaO \cdot SiO_2 \cdot CaCl$.) Identification and composition doubtful.

With a gram of SiO_2, 15 grams $CaCl_2$, and 3 grams NaCl the **chlorosilicate,** round grains of **tridymite**(?), and long prisms of **wollastonite**(?) were obtained. Product treated with dilute acetic acid (1 : 20) and analyzed gave, after deducting 12.7% tridymite, SiO_2, 52.1%; CaO, 47.9%. **Wollastonite** had high birefringence, plane of optic axes horizontal, positive, one axis strongly inclined, density = 2.8–2.9, hardness = 3.5. The formation of wollastonite was doubted by Doelter (43, p. 120, footnote). An **orthosilicate** was also obtained, identification doubtful. When some $MgCl_2$ was present, transparent crystals of a **pyroxene** were obtained, extinction angle = 39°. White *clay* with $CaCl_2$, fused in a current of moist air, gave a **tetrahedral silicate** whose composition was probably $\mathbf{6CaO \cdot 3Al_2O_3 \cdot 3SiO_2 \cdot 2CaCl_2}$. The same melt pulverized and heated a short time with sugar solution gave an insoluble residue of isotropic crystals, in trapezohedra and octahedra, probably **grossularite**(?).

1887 40 LEMBERG, J.: Zur Kenntnis der Bildung und Umbildung von Silicaten, *Z. deut. geol. Ges.*, **39**, 559–600. *Kaolin* treated 190 hours at 200–220° with strong $Na_2O \cdot nSiO_2$ solutions, *n* ranging from 1–4, gave chiefly columnar and roundish kernels of a mineral similar to **analcite,** which when treated with KCl solution at 210° gave **leucite.** By using $2NK_2O \cdot SiO_2$ solution at 210–220°, **indeterminable bundles** or sheaves were obtained, which on treating with NaCl + Na_2CO_3 solution at 210–220° gave isometric crystals of **analcite.** *Kaolin* with NaOH solution gave approximately the composition: $4(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) + 5H_2O$, in which the Na_2O could with difficulty be replaced by K_2O. *Kaolin* treated 190 hours with 20% K_2CO_3 solution at 220–230° gave hexagonal tablets of **kaliophilite;** with Na_2CO_3 for 200 hours at 220°, a **cancrinite** powder.

By the action of Na_2CO_3 solution at 200°, *feldspars* were changed into **analcite,** the action being more rapid the higher the SiO_2 content. *Anorthite* gave a **cancrinite-like** product. *Fused feldspars* with K_2CO_3 solution at 100° gave products resembling **chabazite,** etc.; at 200° the products contained more Na_2O and H_2O, similar to those obtained with *phillipsite, leonhardite,* and *fused analcite.*

Scapolites treated at 100–240° with various solutions gave products similar to **zeolites,** poorly crystallized. *Prehnite* with 14% K_2CO_3 solution, 390 hours at 210–220°, gave columns of a **zeolite-like product;** 16% Na_2CO_3 gave a **cancrinite** containing CaO and Na_2O. *Scolecite* with NaCl in 1 month at 100° gave a **natrolite,** which was reconverted into **scolecite** by 20% $CaCl_2$ solution in 170 hours at 220°. *Fused scolecite* with 18% K_2CO_3

solution, 396 hours at 210–215°, gave an unknown product which, with 16% Na_2CO_3 solution, 174 hours at 210–220°, gave **cancrinite;** with Na_2SO_4 or NaCl, at 220°, **analcite.** *Fused natrolite* gave similar products.

In addition to the above a large number of experiments were made (at temperatures from 100–230°) in which *thomsonite, spodumene, jadeite, andesine, labradorite,* and *albite* were heated with various salt solutions, and the products, which were chiefly amorphous, were carefully analyzed. All these minerals were more or less transformed, generally with addition of H_2O; the composition of the product was often similar to **analcite,** and often the salt used was taken up, producing a compound similar in composition to the members of the **cancrinite-sodalite** group. An interesting point was that fused minerals often gave products different in composition from those obtained with the natural mineral.

1888 41 LEMBERG, J.: Zur Kenntnis der Bildung und Umwandlung von Silicaten, *Z. deut. geol. Ges.*, **40**, 625–56. *Haüynite* and *sodalite* treated with $MgSO_4$ or $CaCl_2$ gave only amorphous products; both were easily decomposed by $MgSO_4$, while the *haüynite* was much more easily decomposed by the $CaCl_2$ than the *sodalite.* A large number of *glasses* made by fusing *oligoclase, andesine, labradorite, natrolite, nepheline, stilbite, leonhardite, prehnite, tremolite* and *wollastonite* were heated with H_2O at about 200°; the amorphous products contained amounts of H_2O from 2.2–30%, mostly about 8–9%. *Kaolin, serpentine* and *pitchstone* were ignited and then heated with H_2O; the products contained considerable H_2O. In addition a number of minerals were heated with K_2CO_3, Na_2CO_3 or K_2SiO_3 solutions, and the products, which were mostly amorphous, analyzed. *Topaz* heated 174 hours at 200–210° with Na_2SiO_3 solution was converted into a **zeolite-like alkali aluminosilicate.**

1889 42 BRUHNS, W.: Beitrage zur Mineralsynthese, *Neues Jahrb. Min. Geol.*, **1889**, II, 62–5. Apparatus a steel bomb, lined with platinum, with cover held down by bolts, and made tight by means of a copper washer, which was protected from the action of the solution by platinum. Freshly precipitated $Fe(OH)_3$ heated for 10 hours with H_2O at 250° gave merely anhydrous amorphous Fe_2O_3. When a trace of NH_4F was added to the same charge, hexagonal plates of **hematite,** 0.03–0.08 mm. long, were obtained, angle about 120°. With Al_2O_3 under similar conditions, at 300°, **corundum,** in pale blue prisms with pyramidal terminations, 0.1 mm. long, were produced, but at 250° the product was amorphous.

Crystals of **quartz,** 0.5–0.8 mm. long, were easily made in a

similar manner from SiO_2, but when *glass* was used a higher temperature was necessary. At 300°, 50 hours were necessary to get **quartz** from K water glass, with Na water glass **quartz** was easily obtained in 10 hours.

Using *microcline*, composition: SiO_2, 64.33%; Al_2O_3, 18.61%; K_2O, 13.49%; Na_2O, 3.56%; and heating for 56 hours at 300° with H_2O containing a little HF, on the walls of the tube were found crystals of **tridymite,** 0.05–0.1 mm. long, in imbricated hexagonal plates. Crystals gave no residue when heated with HF, and gave the reactions of SiO_2(Na_2SiF_6, silica skeleton). On the platinum cover was a crust of large (0.5 mm.) crystals, isotropic, of the form of K_2SiF_6, cubes with octahedral faces. Insoluble in H_2O, qualitative examination gave SiO_2, K, F, Al_2O_3. The other end of the tube gave unchanged feldspar. Attempts to crystallize TiO_2 and SnO_2 failed, but **ilmenite** and **magnetite** were obtained by heating metallic iron, iron oxide, and amorphous TiO_2 in a platinum tube with HF for 24 hours at 270–300°.

1890 **43** DOELTER, C.: Ueber die künstliche Darstellung und die chemische Constitution einiger Zeolithe, *Neues Jahrb. Min. Geol.*, **1890**, I, 118–39. Worked either in a closed nickeled gun-barrel or in a silver-lined steel tube. **Apophyllite** was recrystallized by heating the powdered mineral for 3 weeks at 150–160° with H_2O charged with CO_2; product in small transparent columns showing a prism with pyramids and base, or the more tabular forms with parallel extinction. This mineral was also prepared by heating *okenite* with K_2SiO_3 solution containing CO_2 for about 30 days at 200°. The *okenite* dissolved completely, and formed several new minerals, **apophyllite** predominating. Crystal forms; base, prism, pyramid, distinct, though microscopic. Some **okenite** was also recrystallized, in small radiating bundles of needles, parallel extinction, little effect on polarized light. **Okenite** heated with H_2O containing CO_2 was recrystallized in fine needles; heated for a long time with $AlCl_3$ and Na_2CO_3 solutions containing CO_2 gave **analcite** in trapezohedra with sharp outlines, and **apophyllite** in small crystals (prism and pyramid), and **chabazite** in rhombohedra.

Chabazite was recrystallized from H_2O containing CO_2 at 150°, product fairly large rhombohedral crystals, angle 93–95°, extremely weak birefringence, extinction angle 20°. The same mineral was also recrystallized from liquid CO_2(?). **Heulandite** was recrystallized from H_2O containing CO_2, heated 11 days at 170°, the large crystals obtained appearing mostly as 6-sided (clinopinacoid) or rectangular (orthopinacoid) with dome and base, the first having extinction angle = 0–20°, cleavage along symmetry plane, weak birefringence. Figure obtained on the clino-

pinacoid showed $2V = 40–50°$, character positive, composition: SiO_2, 58.90%; Al_2O_3, 14.02%; CaO, 8.53%; H_2O, 15.19% (by difference) (analysis made on 0.3 gram). **Heulandite** was also synthesized by heating *anorthite* with freshly precipitated SiO_2 gel in H_2O and CO_2 at 200° for 14 days. The product contained, besides unchanged anorthite, **heulandite,** showing both rectangular and 6-sided tablets, the first with parallel, the second with inclined extinction (less than 20°), low birefringence, axial angle measured approximately in one case was 50°, cleavage parallel to plane of symmetry. **Chabazite**(?) was also obtained in this experiment.

Analcite was easily synthesized in characteristic trapezohedra from SiO_2, Al_2O_3 and Na_2O in H_2O at 100–200°. **Natrolite** was recrystallized from H_2O containing CO_2 at 160° in bundles of prisms with pyramidal termination, cross section showed parallel extinction, medium birefringence. Also recrystallized from $NaHCO_3$ solutions. Attempts to prepare it from *nepheline* and SiO_2 at 300° and from *nepheline* and alkali carbonate at 200° failed; **analcite** was obtained in the latter case. **Scolecite** could be recrystallized as above, as unsatisfactory prisms or bundles of needles similar to the natural mineral. *Scolecite* was but slightly decomposed by H_2O at 80°, with 10% Na_2CO_3 it was 43.9% decomposed with enrichment of the solution in SiO_2.

1890 44 FRIEDEL, C. AND GEORGES: Action de alcalis et des silicates alcalins sur le mica: production de la nepheline, de l'amphigène, de l'orthose, *Bull. soc. min.*, **13**, 129–39. By heating at 500° *muscovite* from Moos, Norway, with ¼–⅔ part KOH and at least 20 parts of H_2O, obtained, besides unchanged muscovite, hexagonal crystals of **nepheline,** optically uniaxial, composition corresponding to ⅓ **kaliophilite** and ⅔ **nepheline.** Using NaOH better crystals were found, 0.5–0.8 mm., density = 2.65, uniaxial, composition corresponding to ¼ **kaliophilite** and ¾ **nepheline.** Using *mica* with the amount of KOH and K_2SiO_3 necessary to form leucite got **orthoclase,** tabular parallel to (010), faces (010), (001), (110), present, Carlsbad twinning, angle (001) ∧ (110) = about 116°, extinction on the intersection between (001) and (010) = 4–5°. With a mixture of 1 part *mica*, 1 part calcined SiO_2, and 0.7 part KOH obtained, besides **orthoclase** and **nepheline,** a few crystals of **leucite,** 1 mm. long, quadratic prisms and pyramids, angles (measured on the goniometer) pyramid ∧ prism = 43°25′. Double refraction negative. In complicated forms, (100), (110), (001) and two pyramids (simple and double pyramids). Various modes of twinning, the simplest parallel (112). Striated on (101) parallel to intersection with pyramid. Density = 2.5. HCl gave pulverent SiO_2.

1890 **45** FRIEDEL, C. AND G.: Action des alcalis et des terres alcalines, des silicates alcalins et de quelques solutions salines sur le mica: production de la néphéline, de la sodalithe, de l'amphigene, de l'orthose, de l'anorthite, *Compt. rend.*, **110**, 1170–8. A summarized account of experiments described in (44), (46), (47), and in addition the following: CaO with *mica* gave the octahedral crystals of an unknown **hydrated CaO-Al_2O_3 silicate** previously obtained. These experiments were at 500°. When $CaCl_2$ was used, besides unchanged mica, **anorthite** was formed, extinction angle = 37°, twinning parallel to (001) bounded by (010) and ($\bar{2}$01), also by (110) and (130). Angles measured on goniometer: (001) ∧ (110) = 114–115°; (001) ∧ ($\bar{1}$30) = 98°. Twinning parallel (010) and ($\bar{2}$01). Density = 2.77; composition: SiO_2, 42.67%; Al_2O_3, 36.44%; CaO, 21.47%. Temperature 500° (?).

1890 **46** FRIEDEL, C. AND G.: Action de alcalis et des silicates alcalins sur le mica (deuxième note); production de l'amphigene et de la sodalithe, *Bull. soc. min.*, **13**, 182–7. Analysis of the **leucite** previously obtained (44). **Sodalite** and **nepheline** were prepared at 500° by the action of NaOH and NaCl solution on *mica*, the NaCl being present in amounts ranging from ⅓–2 times the weight of mica used. **Sodalite** crystals, rhombic dodecahedra and cubes, twinning parallel to (211), often elongated parallel to an axis of the cube. Optically isotropic, gave gelatinous SiO_2 with acids, density = 2.32, color grayish, composition: SiO_2, 36.75%; Al_2O_3, 32.41%; Na_2O, 25.75%; K_2O, 0.47%; Cl, 6.36%. The same Cl content was obtained with quite different amounts of NaCl; the formula was probably $3(2SiO_2 \cdot Al_2O_3 \cdot Na_2O) \cdot 2NaCl$. Experiments with 6 grams SiO_2, 5.15 grams Al_2O_3, 3.6 grams Na_2CO_3 and 1.95 grams NaCl, corresponding to this formula, gave only **isotropic globulites.** *Mica* and CaO gave small octahedra of an unknown mineral. See (47) for amounts of material and composition of the product.

1890 **47** FRIEDEL, C. AND G.: Action de la chaux et du chlorure de calcium sur le mica, *Bull. soc. min.*, **13**, 233–7, and Action de la soude et du sulfate de sodium sur le mica, *idem*, pp. 238–41.

In the first article an analysis of the octahedral mineral mentioned in the last two sentences of the abstract (46) leads to the formula $\mathbf{4CaO \cdot 2Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O}$. The mineral was prepared by treating 6 grams of *mica* with 5 grams of CaO.

Two further experiments at 500° are described in which the following materials were used: (1) 6 grams of *mica*, 4 grams of $CaCl_2$, and 0.6 gram of CaO. (2) 12 grams of *mica*, 10 grams of $CaCl_2$, and 3 grams of CaO. In both experiments twinned **anorthite** was produced. The crystals, which are illustrated by

drawings, are diamond-shaped and truncated rectangular tablets. The principal faces that are shown are (001), ($\bar{2}$01), and (010); (110) and (021) are subordinate faces. Angles between pairs of these faces were measured and the values compared with the theoretical ones for anorthite. The extinction angle for most of the crystals was 37°.

The **anorthite** crystals were separated from the unaltered mica by means of a sieve and methylene iodide. Density = 2.77. Composition: SiO_2, 42.67%; Al_2O_3, 36.44%; CaO, 21.47%. Decomposed by acids with separation of silica.

Anorthite was not obtained with CaO alone, and only a few small crystals were obtained when $CaCl_2$ was used alone. The authors suggest that CaO might produce anorthite from mica without the aid of the chloride, if given sufficient time.

In the second article (pp. 238–41) they describe the formation of a **hydrated nosean** which was obtained by heating for 3 days at 500° C. 6 grams of *mica*, 3 grams of NaOH, and 6 grams of $Na_2SO_4 \cdot 10H_2O$. The product was in hexagonal prisms, (10$\bar{1}$0), (11$\bar{2}$0) with pyramid (10$\bar{1}$1). The crystals are deeply striated parallel to the *c*-axis, i.e., parallel to their length. Angles in the prism zone, 30°, 60°, 90°. Optically negative, uniaxial, low birefrigence, normal angle between two pyramidal faces = 24°22.7′. Other angles were calculated and compared. Analysis: SiO_2, 34.81%; Al_2O_3, 29.91%; SO_3, 7.25%; Na_2O, 23.34%; H_2O, 3.95%; formula $3(Na_2O \cdot Al_2O_3 \cdot SiO_2) + Na_2SO_4 + 2H_2O$. Besides these crystals, brown hexagonal lamellae, uniaxial, negative, density that of mica, not appreciably attacked by HCl, were found. Since the original material contained MgO, this was probably **biotite.** Experiments with added MgO were without result.

1890 **48** CHROUSTSCHOFF, K. VON: Reproduction de l'amphibole, *Compt. rend.*, **112**, 677–9; *Neues Jahrb. Min. Geol.*, **1891**, II–86–90; Über künstliche Hornblende, *Acad. Sci. St. Petersburg*, **34** (2), 1891–92, 187–92. Worked in thick-walled evacuated glass tubes, volume 25 cc., heated for 3 months at 550°, using a mixture of colloidal SiO_2 solution, colloidal $Fe(OH)_3$, colloidal $Fe(OH)_2$, lime water, freshly precipitated $Mg(OH)_2$, and several drops of a NaOH-KOH solution. Product contained, among other things, long, thin dark-colored prismatic crystals of **hornblende,** 1 mm. long, 0.5 mm thick, faces (010), (110), (011) visible; angle (110) $\wedge$ (1$\bar{1}$0) could only be approximately measured, angle (011) $\wedge$ (0$\bar{1}$1) = 148°28′. Cleavage indistinct, extinction *c*: Z_{NA} = 17°56′, optical character negative, pleochroism Z bluish green, Y yellowish green, X pale yellowish green, dispersion $\rho < v$; $\gamma - \alpha = 0.025$, mean index = 1.628, 2V = about 82°, $d_{15°}$ = 3.2452, composition: SiO_2,

42.35%; Al_2O_3, 8.11%; Fe_2O_3, 7.91%; FeO, 10.11%; MgO, 14.33%; CaO, 13.21%; Na_2O, 2.18%; K_2O, 1.87%; ignition (H_2O), 0.91%. Also found light prismatic green crystals, faces (110), (100) visible, rarer (010), and dome terminations, mean index = 1.65, extinction partly parallel, partly at angle = 37°, $\gamma - \alpha = 0.027$, optical character positive, apparently a **diopside-like pyroxene.** Also found colorless grains and crystals, poorly developed, faces (100) visible, isotropic, possibly **analcite**(?). Other minerals were **quartz,** 0.2 mm. crystals, faces ($10\bar{1}1$), ($01\bar{1}1$), ($10\bar{1}0$); and thin flakes resembling **adularia.** (Probably **orthoclase,** at 550°.)

1891 **49** FRIEDEL, G.: Production du corindon et du diaspore par voie humide en liqueur alcaline, *Bull. soc. min.*, **14**, 7–10. Corundum and diaspore could not be prepared by heating in a bomb a solution of NaOH saturated at boiling with Al_2O_3, but were obtained when excess Al_2O_3 was present. The amount of excess Al_2O_3 was without influence; **corundum** only was obtained at 530–535°, both at 450–500°, and **diaspore** only at 400°. If SiO_2 was present it crystallized as **quartz.** The **corundum** was in short reddish uniaxial negative rhombohedra; with slight Al_2O_3 excess at 530° with ($22\bar{4}3$). The angle between two faces in this form (normal angle) was 51°40′. The reddish color was ascribed to the presence of a little Cr_2O_3. The **diaspore** was in colorless flat prisms, with rectangular outline, often with curved faces, with angles 105° to cleavage plane. Not attacked by acids. Birefringence small, biaxial, axial plane parallel to cleavage plane. When CaO was present **calcite** was found; SiO_2 crystallized as **quartz. Hematite** was obtained from Fe_2O_3 at from 450–500° in hexagonal lamellae; below 280° only amorphous powder was found; no göthite.

1891 **50** FRIEDEL, C. AND G.: Action du sulfate de sodium et du carbonate du sodium sur le mica en présence de la soude, *Bull. soc. min.*, **14**, 69–75. By heating *mica* with NaOH and Na_2SO_4 solution at 500(?) obtained a **nosean** containing a small amount of H_2O, rhombic dodecahedra modified by the faces of a cube, isotropic, density = 2.28, easily attacked by dilute HCl, composition: SiO_2, 32.43%; Al_2O_3, 31.13%; SiO_2, 7.61%; K_2O, 4.24%; Na_2O, 20.13%; H_2O, 2.32%; cf. (47); the difference was ascribed to the fact that the bomb leaked during this experiment. A **cancrinite-like mineral** was obtained with 14 grams *mica*, 7 grams NaOH, 14 grams Na_2CO_3, and H_2O at 500°, formula $3(2SiO_2 \cdot Al_2O_3 \cdot Na_2O) \cdot Na_2CO_3 \cdot 2H_2O$, crystals hexagonal, with prism and pyramid, angle of the pyramidal face = 23°49′ − 25°1′, density = 2.35, optically negative, birefringence = 0.010.

1891 **51** FRIEDEL, G.: Production artificielle de la brucite, *Bull. soc. min.*, **14**, 74. **Brucite** was obtained as colorless hexagonal micaceous

flakes by the action of NaOH solution on MgO at 400°; uniaxial, positive, high birefringence. Additional note G. Friedel. *Ibid.*, **14**, 194–5.

1891 **52** GRAMONT, A. DE: Production artificielle de la datholite, *Compt. rend.*, **113**, 83–4. Used apparatus of Friedel; charge an intimate mixture of 25 grams borax and 5 grams precipitated $CaSiO_3$, heated for 36 hours at 400° in the presence of H_2O. Product a mixture of amorphous material, **wollastonite,** a **crystalline powder** in crystals too small for optical determination, and **datolite,** in crystals having the appearance of being monoclinic, with extinction angle very small, strong birefringence. Fouqué pronounced the crystals optically negative. Composition: SiO_2, 35.39%; CaO, 35.95%; H_2O, 6.65%; FeO, 1.19%; B_2O_3, 20.82%. The same crystals were also obtained by the action of Na_2SiO_3 solution on K borax at 300°.

1892 **55**

1891 **53** FOUQUÉ, F., AND MICHEL-LÈVY, A.: Reproduction artificielle d'un trachyte micacé, *Compt. rend.*, **113**, 283–5. Used 1.5 grams of a *glass* made by fusing a *granite* from Vire, with 6 drops H_2O, heated at red heat, product merely sintered together. In the center of the clumps was some white crystalline material, not attacked by acids, containing SiO_2, Al_2O_3, K_2O, Na_2O and CaO, under the microscope showed the habit of **orthoclase. Spinel** and **biotite**(?) were also found.

1892 **54** THUGUTT, STANISLAUS JOSEPH: Mineralchemische Studien, *Zeit. anorg. Chem.*, **2**, 64–107, 113–56. The following experiments were all at about 200°. By the action of 16.8 grams NaOH dissolved in 105 cc. H_2O on 35 grams *kaolin*, a hydrated nepheline, $4(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot 5H_2O$, was obtained in orthorhombic crystals, low birefringence, parallel extinction, dominant faces (100), (010), (001), twinnings and fourlings. Fatty acids aided the crystallization. Attempts to prepare substituted members of the sodalite group from the *hydrated nepheline* or from *kaolin* generally resulted in amorphous products, which were carefully analyzed. In a few cases the above **hydrated nepheline** was obtained; also amorphous **Li nepheline;** and occasionally a few poorly formed crystals of **unknown minerals.** *Kaolin* treated with phenol solution was partially decomposed; treated with 47% KOH *kaolin* gave an amorphous product; and treated with 1% NaOH gave clear birefringent needles, composition corresponding closely to $\mathbf{4(Na_2O \cdot Al_2O_3 \cdot 3SiO_2) \cdot 15H_2O}$. Treated with alkaline silicate solutions of different concentrations *kaolin* gave, besides amorphous products, **needles** and **globulites** containing H_2O and more SiO_2 than the kaolin. *Kaliophilite* treated with 1% K_2SiO_3 solution gave **needles** with parallel extinction, composition: SiO_2, 46.88%; Al_2O_3, 22.00%; K_2O, 19.87%; H_2O, 11.25%; other similar experi-

1894– **56**

ments gave partly amorphous, partly crystalline products. *Corundum* treated with H_2O alone was little altered, 4.5% H_2O was taken up; treated with alkaline solutions after ignition *corundum* was partly altered to amorphous products. *Diaspore* was little altered by H_2O alone; with a solution of K_2SiO_3 it was partly altered to crystals with inclined extinction, combinations of (110), (100), (001), (hk0); samples for analysis could not be isolated. Several natural *glasses* took up a small amount of H_2O when heated with H_2O.

1892 **55** CHROUSTSCHOFF, K. VON: Über künstliche Hornblende, *Bull. acad. sci. St. Petersburg*, (2) **34**, 187–92. Apparatus was a 3-piece iron bomb lined with platinum and closed by a screw and copper washer.

Expt. I. Used mixture of SiO_2, $Al(OH)_3$ and $Zr(OH)_4$, all in gelatinous form, heated for 12 hours, final temperature a red heat. All H_2O was lost in this experiment. Product amorphous and in **thin flakes,** with occasional pyramids and prisms, largest 0.035 mm., average 0.012 mm., low birefringence, extinction parallel to 2 sides of the hexagon (consequently mineral was not hexagonal), density = 2.87, composition: SiO_2, 53.65%; Al_2O_3, 23.76%; ZrO_2, 14.54%; H_2O, 7.86%.

Expt. II. Bomb remained tight. Used gelatinous SiO_2 and $Zr(OH)_4$, product contained **zircon,** faces (111), (221), (311), (101), (110), (100) visible, birefringence high, most crystals developed in pyramids (111), a few had long prismatic habit (111), (110), a few short prismatic, (111), (110). Crystals (111), (110), (100), rare, (101) and (221) and ditetragonal pyramids very rare. $D_{12°} = 4.4537$, composition: SiO_2, 32.84%; ZrO_2, 67.17%.

1894–5 **56** THUGUTT, ST. J.: Zur Chemie einiger Alumosilicate, *Neues Jahrb. Min. Geol., Beil. Bd.*, **9**, 554–624. The orthorhombic **hydrated nepheline** previously obtained (54) was heated with various solutions and the replacements studied. When 5 grams were heated with 500 cc. 2% K_2CO_3 solution for 95 hours at 186–191°, and later for 96 hours at 196–202° with fresh solution, 0.528 gram Al_2O_3 went into solution, while the composition of the mass, composed of globulites and a few weakly birefringent needles, was that of a **K natrolite.** *Hydrated nepheline* with H_2O gave product similar to **nacrite.** When **Na anorthite,** obtained by fusing the *hydrated nepheline*, was heated 98 hours at 174–177°, then 97 hours at 205–211°, with 2% K_2CO_3 solution, the solution contained ⅓ of the Na_2O and Al_2O_3, and needles of **K natrolite** were obtained. *Kaliophilite* when heated with H_2O for a long time at 196–230° gave a **micaceous product** and an alkaline solution. A blue *chloride-sodalite* (from nepheline syenite from Ditró) with 2%

K_2CO_3 solution at 192–195°, then at 211–214°, gave needles of **K natrolite,** and a solution containing NaCl, NaOH and Al_2O_3. Similar experiments were made on various *sodalites* with similar results.

Nepheline with 2% K_2CO_3 solution gave in part **natrolite,** with separation of **iron oxide.** *Nepheline* with H_2O at 200° gave a product similar to **potash mica,** and Al_2O_3 in solution. *Kaolin* (2 grams) at 192–202° with 190 cc. 2% KOH solution gave "**K natrolite,**" with Al_2O_3 in solution. *Kaolin* (3 grams) with 190 cc. 1% NaOH solution gave needles of the composition $\mathbf{Na_6Al_6Si_8O_{28}\cdot 5H_2O}$. At 100° different products were obtained, and much more SiO_2 and Al_2O_3 went into solution. *Sanidine* (2.8 grams) with 1–2% KOH solution showed no effect. By the action of dilute K_2CO_3 solution on members of the *sodalite* and *nepheline* groups at 174–211° **K natrolite** was formed, which when heated on the steam bath with 5% Na_2CO_3 solution gave "a silicate $Na_2Al_2Si_3O_{10}\cdot 4H_2O$, a **hydrated Na natrolite.**"

More experiments (at 200°) in which **analcite** and **leucite** are converted into each other are given. When 15.3 grams $NaAlO_2$ and 7.3 grams NaOH and 3.7 grams Na_2CO_3 were dissolved in H_2O, the clear solution diluted to 130 cc. and heated 79 hours at 184–190° with 3.7 grams CO_2, most of the Al_2O_3 separated was amorphous, but some **diaspore** in birefringent needles with sharp terminations and parallel extinction was found, as well as a little **dawsonite.**

1895 57 CHROUSTSCHOFF, K. VON: Über reguläre Kieselsäurekrystalle, *Bull. acad. sci. St. Petersburg,* **1895,** 27–33. Using amorphous SiO_2 with HBF_4 and H_2O in a platinum-lined bomb found no change below 180°; from 180–228° got isometric crystals of **cristobalite,** density = 2.412, faces (111), (100), (110) visible, isotropic, refractive index = 1.48, soluble in HF, 99.78% SiO_2; from 228–235° got no quartz; 240–300° **quartz;** 310–360° **tridymite** and **quartz.**

1895 58 SPEZIA, GIORGIO: La pressione nell'azione dell'acqua sull'apofillite e sul vetro, *Atti accad. sci. Torino,* **30,** 455–65. H_2O under a pressure of 1750 atmospheres at ordinary temperature had no action on *apophyllite,* at 93–107° and 500 atmospheres there was no marked action, but H_2O at 190–211° under the normal pressure for that temperature strongly corroded the mineral in 13 days. *Glass* behaved in a similar manner.

1896 59 FRIEDEL, G.: Sur un nouveau silicate artificiel, *Bull. soc. min.,* **19,** 5–14. When *muscovite* was treated with 10% NaOH solution at 200° only **nepheline** was formed and the action was slow. At 500° with 2% NaOH the action was more rapid, and **nepheline** and a new mineral (**sodium thomsonite**(?)) were formed. With but little SiO_2 present, **nepheline** only was found; when the $Na_2O : SiO_2$

1896 60

1896 61

1896 62

ratio was 1 : 1, **nepheline** and **analcite** were found; with ratio 1 : 2 or 1 : 3, no nepheline, but **analcite** and **albite;** with ratio 1 : 4 and over, only **albite** and **quartz** were obtained. The **new silicate** was best obtained when 4–5 grams *muscovite* were heated with 40 cc. 8–10% NaOH solution at 500–530°. It was easily attacked by HCl, composition: SiO_2, 40.78%; Al_2O_3, 36.73%; Fe_2O_3, trace; CaO, 0.15%; Na_2O, 15.40%; K_2O, 1.88%; H_2O, 4.93%, crystals orthorhombic, colorless, $d_{18°} = 2.378$, crystal form similar to that of olivine, (110), (001), (010), (201) visible, twinning parallel (110), fourlings, angles, measured on goniometer, $(110) \wedge (1\bar{1}0) = 114°20'$, $(110) \wedge (010) = 122°50'$, $(001) \wedge (021) = 136°30'$, $(010) \wedge (021) = 133°30'$. On (001), (010) weak birefringence, negative on (010), positive on (001), β perpendicular (100), γ perpendicular (001), α perpendicular (010), $\beta - \alpha = 0.0018$, $\gamma - \beta = 0.0017$, $\beta = 1.52$, axial angle about 88°, acute negative bisectrix α. Heating experiments were also made on the new mineral, from which it was concluded that the H_2O was in solid solution. This mineral could not be obtained with a greater SiO_2 content. **Na cancrinite** was also found, due to Na_2CO_3 in the NaOH. *Cf.* (66) and (67).

1896 **60** FRIEDEL, G.: Sur des figures de corrosion du mica et sur l'orientation des fissures de glissement produites par la perforation, *Bull. soc. min.*, **19**, 18–22. Describes the etch figures on *muscovite* remaining after preparation of **sodalite,** using 5 grams NaOH, 3 grams NaCl and H_2O at 300°.

1896 **61** SCHULTEN, A. DE: Reproduction artificielle de l'hydrargillite, *Bull. soc. min.*, **19**, 157–61. Saturated ammoniacal $Al(OH)_3$ solution was heated on a sand bath 15 days, in such a manner that the NH_4OH only slowly escaped, and **hydrargillite** was obtained. **Hydrargillite** was also obtained better crystallized by slow precipitation from a solution prepared by dissolving 25 grams Al in 75 grams NaOH dissolved in 400 cc. H_2O, by passing CO_2 through the boiling solution. Product contained 64.47% Al_2O_3, 34.76% H_2O, 0.53% SiO_2; $d_{15°} = 2.423$, slowly attacked by boiling HCl or H_2SO_4, crystals glittering monoclinic prisms, 0.3 mm. long, faces (100), (110), (001) visible, cleavage parallel to (110), angles $(110) \wedge (010)$ and $(110) \wedge (1\bar{1}0)$ about 120°, monoclinic, angle of extinction with plane of prism = 20°, optically positive, twinning parallel to (100).

1896 **62** SPEZIA, GIORGIO: La pressione nell'azione dell'acqua sul quarzo, *Atti accad. sci. Torino*, **31**, 246–50. Found that plates of *quartz* kept at 27° for several months with H_2O under a pressure of 1750–1850 atm. did not diminish in weight and showed no etch figures. Pressure alone has no influence on the solubility of quartz.

1897 **63** LUNGE, G., AND MILLBERG, C.: Über das Verhalten der verschiedenen Arten von Kieselsäure zu kaustischen und kohlensauren Alkalien, *Zeit. angew. Chem.*, **13**, 393–8, 424–31. A summary of the older work on the solubility of the various forms of SiO_2, and many original experiments on the solubility of *quartz*, *opal* and amorphous SiO_2 in boiling alkaline and carbonate solutions.

1898 **64** SPEZIA, GIORGIO: Esperienze sul quarzo e sull'opale, *Atti accad. sci. Torino*, **33**, 289–308, 876–82. The solubility of *quartz* in H_2O does not depend on the pressure but only on the temperature. By slow evaporation of solutions containing SiO_2, **opal** was deposited, but when alkali was present the SiO_2 separated as **quartz.** The rhombohedral faces of *quartz* were most easily attacked, and on the same faces there was the greatest deposit of SiO_2 from Na_2SiO_3 solutions. The more rapid growth of quartz crystals in the direction of the vertical axis explains the common prismatic form of the mineral. These directions of maximum and minimum rate of growth of quartz, respectively parallel and perpendicular to the vertical axis, were confirmed by experiments on crystals cut in various directions. *Opal* treated in the same way was changed to an aggregate of **quartz** crystals.

1898 **65** BARUS, C.: Remarks on colloidal glass, *Am. J. Sci.*, [4] **6**, 270. Announces the impregnation of *glass* with H_2O to such an extent that it melted below 200°, the solution occurring with a contraction in bulk. Heated in the air the hydrous glass swelled enormously with loss of H_2O, leaving a white, porous **pumice** resembling pith.

1899 **66** FRIEDEL, C.: Analyse d'un silicate d'aluminum et de sodium artificiel, *Bull. soc. min.*, **22**, 17–18. New analysis of G. Friedel's preparation in (59). Composition: SiO_2, 39.98%; Al_2O_3, 32.95%; Na_2O, 19.09%; K_2O, 3.19%; H_2O, 5.80%. Composition: $NaAlSiO_4 \cdot 0.5H_2O$, resembles **thomsonite,** but all the CaO is replaced by Na_2O and the H_2O content is different. See (59) for description and conditions of formation.

1899 **67** FRIEDEL, G.: Sur un nouveau silico-aluminate artificiel, *Bull. soc. min.*, **22**, 20–25. By heating 5 grams *muscovite* with 40 cc. 9% NaOH solution for 36 hours at 508–510° obtained **nepheline,** the **new silicate** described (59), and another **new silicate.** The latter was only obtained once, occurs as colorless isometric crystals; $d_{12.5°} = 2.660$; forms observed octahedra, rhombic dodecahedra, trapezohedra, and cubes. Probably hemihedral-tetrahedral, but optically abnormal. Birefringence = 0.0046, extinction = 5–6°, strongly twinned, single individuals monoclinic, composition: SiO_2, 41.92%; Al_2O_3, 26.43%; CaO, 0.25%; Na_2O, 31.25%; formula $\mathbf{8SiO_2 \cdot 3Al_2O_3 \cdot 6Na_2O}$. Crystal figures are given.

1900 **68**

1900 **69**

1901 **70**

1900 **68** SPEZIA, GIORGIO: Solubilità del quarzo nelle soluzioni di silicato sodico, *Atti accad. sci. Torino*, **35**, 750–61. Dilute solutions of Na_2SiO_3 exerted a decided solvent action on *quartz* at high temperature; at lower temperature the **quartz** was deposited.

1900 **69** BARUS, C.: Hot water and soft glass in their thermodynamic relations, *Am. J. Sci.*, [4] **9**, 161–75. Cf. (65). An ordinary soft *glass* was heated with H_2O in a steel bomb, using 210 grams of the finely powdered glass and 50 grams H_2O, and heating at 210° for 12 hours. Product hard and opalescent, and homogeneous except for some inclusions of partially converted glass. Heated in the air it swelled enormously with loss of H_2O, forming a white pith-like mass; left in the air it gradually broke up, probably due to the effect of internal stress. When 180 grams of this product was heated to 210° with 50 cc. H_2O more H_2O was taken up, and the glass changed to a friable mass which did not swell up when heated; about 10 cc. of viscous soapy black solution was left in the bomb. Repetition of this treatment gave a similar result. When the action was observed in a capillary tube under pressure (applied by means of a Hg column) the phenomena were different at different temperatures. At 185° the *glass* of the tube absorbed H_2O, swelling enormously, and became white and turbid. At 210°, however, solution took place rapidly, forming a clear liquid, and while solution was taking place the compressibility was very large, but fell suddenly at the end. When a solution of $Co(NO_3)_2$ was used the glass acted as a semi-permeable membrane, only taking up the H_2O.

1901 **70** FRIEDEL, G.: Sur un silicate de lithium cristallisé, *Bull. soc. min.*, **24**, 141–59. *Muscovite* heated with 5% LiOH solution in a closed bomb at 500° gave an amorphous product; *lepidolite* from Rozena similarly treated was but slowly attacked, but (1) large trigonal prisms of a **Li silicate,** (2) cubes of **LiF,** and (3) small amounts of **unknown crystals,** were obtained. *Lepidolite* was rapidly attacked by NaOH, producing the above **Li silicate** without admixture of other bases, and **Na-K nepheline** free from Li. When carbonate was present, Li-free alkali **cancrinite** was found. Li aluminosilicate cannot be prepared in this manner. The **Li silicate** was prepared by heating at 500° a LiOH solution with excess amorphous SiO_2; product, water free; composition: SiO_2, 67.1%; Li_2O, 32.9% = Li_2SiO_3; crystal form similar to phenacite; colorless; rhombohedra of 116°7′ predominating, also prisms $(11\bar{2}0)$, $(10\bar{1}0)$, and (0001) common, $(12\bar{3}2)$ and $(22\bar{4}3)$ frequent, (1232) hemihedral. $D_{15°} = 2.529$, mineral uniaxial, positive, minimum refractive index = 1.65, birefringence = 0.020. On account of the resemblance of the mineral to phenacite, LiOH and NaOH solu-

tions were heated with BeO and SiO_2 at 500°; product both **Li_2SiO_3** and **phenacite,** no isomorphous mixture. The Li orthosilicate could not be prepared, but Li_2SiO_3 took up SiO_2 in solid solution.

1902 **71** BAUR, EMIL: Ueber die Bildungsverhältnisse von Orthoklas, *Zeit. physik. Chem.*, **42**, 567–76. Worked at 520° in a steel cylinder closed by a conical screw cap.

Expt. No.	SiO_2 g.	$KAlO_2$ g.	Product
1	5	2.0	**Quartz** and an **unknown mineral in radiating clusters,** $n = 1.65$, birefringence = 0.015. Optically positive, axial angle small, elongate perpendicular to plane of axes.
2	5	3.3	**Quartz** and globulites of **orthoclase.**
3	5	5.0	**Quartz, orthoclase,** sections of which perpendicular to r showed large axial angle, extinction angle = 5°, refractive index lower than Canada balsam, birefringence weak, Carlsbad twinning.
4	5	15.0	**Orthoclase,** in plates with unequal 6-sided border, showing a large axial angle perpendicular to positive bisectrix, elongation α, formed a very small angle with an edge.
5	5	25.0	Mostly amorphous, but a few **undeterminable needles** that gelatinized with HCl.
		$NaAlO_2$	
6	13	4.5	**Quartz**
7	5	2.3	**Quartz**
8	5	4.3	**Quartz, albite** showing twinning, refractive index less than Canada balsam; **tridymite** in tablets composed of many individuals variously oriented, refractive index lower than Canada balsam, weak birefringence, small axial angle, optically positive.
9	5	10.0	**Albite,** with characteristic refractive index and birefringence, elongate along a axis, optical character of chief zone negative, twinning lamellæ parallel to chief zone, extinction angle very small, chief face approximately parallel to plane of axis.
10	5	15.0	Both experiments gave crystals which gelatinized with HCl, and had most of the characteristics of **nepheline,** but did not correspond to any known mineral. Rectangular tablets, refractive index slightly higher than Canada balsam, acute bisectrix perpendicular to observed faces, large axial angle. Elongation α, birefringence at least 0.015; parallel extinction.

1906 **72** ALLEN, E. T. (cited by Day and Shepherd): *Am. J. Sci.*, [4] **22,** 297. Very fine **quartz** crystals were obtained by heating a solution of $MgCl_2 \cdot 6NH_4Cl$ and Na_2SiO_3 for 3 days at 400–450°. Large crystals 2 mm. long, often barrel shaped, with short rhombohedral terminal faces, striations horizontal.

1906 **73** DOELTER, C.: Minerogenese und Stabilitätsfelder der Minerale, *Min. petr. Mitt.*, **25**, 79–112. Used a tube similar to that used by Sarasin, 11 grams of a mixture of $CaHCO_3$ and precipitated SiO_2, with 45 cc. H_2O at 400–425°; product **wollastonite** in strongly birefringent biaxial crystals; maximum extinction angle = 30°; partly in long flakes, partly in radiating groups; soluble in hot concen-

trated HCl; insoluble in dilute HCl. Analysis of some crystals having a surface coating of SiO_2 gave: SiO_2, 55.01%; H_2O, 0.91%. Density = 2.75, hardness = 4.5. From 4 grams of a mixture of KOH, SiO_2 and $Al(OH)_3$ in proportion of $KAlSi_3O_8$, heated for 8 days at 400°, obtained numerous crystals corresponding to **orthoclase.** From 2.5 grams *analcite* and 2.5 grams of a mixture of $NaAlO_2$ and SiO_2 in proportions of analcite, plus 1 gram $NaAlO_2$ and 60 cc. H_2O, heated 110 hours at 430° obtained a few hexagonal tablets of **nepheline,** twinned lath-like crystals resembling **albite,** and a few high index crystals resembling **corundum.**

Analcite was obtained at 200° from *nepheline*, H_2O, alkali carbonate, and CO_2. An experiment using 6 grams of pure analcite mixture and 30 cc. H_2O at 400° gave hexagonal flakes probably of **nepheline** and much **analcite** in trapezohedra. Two experiments at 90° with 60 cc. H_2O, the first with 5 grams of a mixture of Na_2CO_3, Al_2O_3, and SiO_2 in analcite proportions, the second 1 gram of a mixture in natrolite proportions, both plus a little *natrolite*, gave **natrolite** in radiating clusters, and an orthorhombic mineral with higher index, probably **diaspore.** At 190°, 3 grams of a mixture of *natrolite* with 70 cc. H_2O, seeded with *natrolite*, gave both **natrolite** and **diaspore;** and at 200° a mixture of the composition of analcite gave **analcite** crystals. Concluded that in concentrated solutions at 90° **natrolite** is formed from a mixture of the composition of natrolite; at 190°, **analcite** from the same mixture; an analcite mixture, seeded with *natrolite*, at 90° gives **natrolite,** and at 190°, **analcite.**

1906 **74** ALLEN, E. T., WRIGHT, F. E., AND CLEMENT, J. K.: *Am. J. Sci.*, [4] **22,** 405. Worked in a steel bomb closed by a copper disc held in place by a screwed-on steel cap, used either $MgCl_2 \cdot 6NH_4Cl$ solution or a mixture of $MgCl_2$ solution with $NaHCO_3$, and either amorphous SiO_2 or Na_2SiO_3. Heated 3–6 days at 375–475°. Obtained **magnetite,** in octahedra; a **Mg amphibole** in aggregates of fibers with parallel extinction, elongation *c*, refractive index below 1.60, birefringence low; **forsterite,** with extinction parallel to prism edge, refractive index about 1.66, much stronger birefringence than either metasilicate or quartz; and **quartz** (cf. (72)).

1906 **75** KÖNIGSBERGER, JOHN, AND MÜLLER, WOLF. J.: Versuche über die Bildung von Quarz und Silikaten, *Centr. Min.*, **1906,** 339–48, 353–72. Worked in a steel bomb lined with Pt-10% Ir alloy, fitted with an apparatus for filtering, and placed in a shaking apparatus. Experiments 1–4 were made with a Thuringian *glass*, composition: SiO_2, 69.21%; Al_2O_3, 2.48%; Fe_2O_3, 0.45%; MgO, 0.52%; CaO, 9.84%; K_2O, 1.98%; Na_2O, 14.91%.

Experiment 1. 8 grams *glass* in pieces 2–5 mm. were heated with 60 cc. H_2O and 2 grams CO_2 for 60 hours at 360°, filtered, and slowly cooled (the same experimental conditions were used in 2, 3, and 4). In filter tube found 0.07 gram **quartz,** in crystals 0.01–0.05 mm., density = 2.63, completely soluble in HF, ratio lengths along *a* (perpendicular to major axis) and *c* was 1 : 2.5; prism faces and one rhombohedral face well formed, other rhombohedral faces rare and small, birefringence fairly strong, refractive index higher than Canada balsam, interfacial angles measured corresponded to those calculated for quartz. The solid residue consisted of (1) **quartz,** 0.05–0.2 mm. long, with prism and rhombohedra, (*a*) : (*c*) = 1 : 3 and 1 : 2, striated perpendicular to the major axis; (2) **chalcedony,** in radial aggregates; (3) some **weakly birefringent aggregates** which could not be identified; (4) **calcite.**

Experiment 2. Used 8 grams *glass,* 60 cc. H_2O, 10 grams CO_2. No noticeable crystallization in the filter tube; glass covered with a white crust of **quartz** and **chalcedony.** The solution contained 2.5% dry substance, 1.3% of which was CO_2, no Al_2O_3 or SiO_2. The temperature was 360° in experiments 2, 3, and 4.

Experiment 3. 8 grams *glass,* 60 cc. H_2O, 15 grams CO_2. No crystals in filter tube; glass but slightly attacked and had a thin coating of small **birefringent particles** and **quartz**(?).

Experiment 4. 10 grams *glass,* 50 cc. H_2O. In filter tube 0.2 gram crystals, chiefly **quartz,** partly in long crystals, (*a*) : (*c*) = 1 : 7, partly short, (*a*) : (*c*) = 1 : 1.5, faces as in Experiment 1; also amorphous SiO_2, with properties corresponding to **opal.** *Glass* completely decomposed, partly changed into amorphous SiO_2; partly into **chalcedony;** partly into **tridymite,** in imbricate hexagonal plates, interfacial angle = 120°, density = 2.3; refractive index little greater than 1.407, soluble in NaOH and HF; partly into **anorthoclase,** showing plates which scratched glass, without symmetry, consequently triclinic, faces (010), ($\bar{2}$01), (110), (111), extinction angle with one side = 3–8°, interfacial angles = 80–81°, and 116–117°, indistinct cleavage often (010), rarer (001), $\alpha = 1.515$ In experiments 5–9 an *obsidian* was used, composition: SiO_2, 74.3%; Al_2O_3, 13.0%; Fe_2O_3, 2.6%; MgO, 0.3%; CaO, 1.0%; Na_2O, 3.8%; K_2O, 4.6%; H_2O, 0.3%.

Experiment 5. 10 grams *obsidian,* 60 cc. H_2O, 48 hours at 320°, filtered, slowly cooled (similar experimental conditions in 6, 7, 8). *Obsidian* little attacked, in filter tube were (1) small **birefringent needles,** (2) small, **red, transparent plates** containing Fe, (3) small isotropic or slightly birefringent **hexagonal crystals.** *Glass* remaining but slightly attacked, some pieces covered with a gray crust of **fine needles** and reddish brown **concretions.**

Experiment 6. 10 grams *obsidian*, 50 cc. H_2O, 15 grams CO_2, 320°. *Obsidian* had thin coating of carbonate.

Experiment 7. 10 grams *obsidian*, 60 cc. H_2O, 3 grams CO_2, 2 grams $NaHCO_3$, 320°. *Obsidian* but lightly attacked, but more than in Experiment 6. A little **quartz** in filter tube; a crust on the *obsidian* composed of same **needles** and **concretions** as before, and also poorly formed **chalcedony** and many small birefringent crystals, probably **quartz.**

Experiment 8. 10 grams *obsidian*, 60 cc. H_2O, 4 grams $NaHCO_3$, 320°. Much more strongly attacked. About 0.3 gram **quartz** in filter tube, similar to that in Experiment 1, with positive and negative rhombohedra generally unequally developed, chiefly with a trigonal trapezohedron ($51\bar{6}1$). Photomicrograph given. In the filter tube were also (1) small brownish red kernels of an **Fe_2O_3 compound,** (2) large thick approximately **hexagonal tablets,** with small birefringence, refractive index probably close to that of Canada balsam, (3) transparent **isometric crystals** showing equal development in all directions. The obsidian residue consisted of well-formed **quartz** crystals, and dark colored amorphous concretions.

Experiment 9. 10 grams *obsidian*, 40 cc. of solution. Composition: H_2O, 85%; CO_2, 5%; Na, 2.5%; K, Li, 1.5%; Ca, 0.3%; CO_3, 3.5%; Cl, 1.5%; SO_4, 0.7%; corresponding to the authors' average composition of the solution from which vein minerals crystallize. Heated to 420° for 42 hours, filtered, slowly cooled, product in filter tube a few **quartz** crystals; residual *obsidian* covered with a thin, grayish green crust, on which were thin radiating aggregates of a dark green silicate, insoluble in concentrated HCl, with clear yellowish green pleochroism, color in direction of γ dark green, direction α light green, extinction angles with elongation = 38°, birefringence strongest in direction of elongation. Needles lying on other faces showed smaller extinction angles and much smaller birefringence. Hardness greater than the obsidian, density = 3.36; treated with HF left a residue containing Fe and Na. Mineral probably a **pyroxene** rich in iron, an **aegirite-augite. Quartz** and thin reddish transparent plates, probably of **hematite,** were also found.

Experiments 10, 11, 12, 13. The following minerals were heated with 40 cc. H_2O for 24 hours at 350°. *Experiment 10. Quartz* showed corrosion on the rhombohedral faces, but no attack was visible on the prism faces. *Experiment 11. Muscovite* was very strongly attacked, chiefly perpendicular to *c*. *Experiment 12. Diopside* was about one-fifth decomposed, the chief effect being parallel to (110), etch figures also obtained on (100) and (010).

Part of the *diopside* was transformed into fine, thin, **white threads.** *Experiment 13.* *Adularia* was not strongly attacked, the greatest effect being parallel to the chief cleavage (010).

Experiment 14. (1) *quartz*, (2) *adularia*, (3) *muscovite*, (4) *granite* were heated 24 hours with 50 cc. of 20% Na_2CO_3 solution at 350° in a silver tube, which did not hold completely tight. The minerals dissolved completely, remaining in solution when cold. (The amount of minerals dissolved was not stated.)

Experiment 15. *Muscovite*, *quartz*, *adularia*, *spinel*, *calcite*, *fluorspar*, and *biotite* were heated to 370° for 48 hours with 60 cc. H_2O, 1 gram Na_2CO_3, and 10 grams CO_2, and filtered. Only a small amount of carbonate was found in the filter tube; the minerals were little attacked, the *calcite* showing the greatest action, and the *muscovite* and *fluorspar* a slight change. Pure 30% NaOH dissolves most silicates at 115°.

From the preceding experiments, Königsberger and Müller draw some conclusions in regard to the acidity of silicic acid, the most important being that the acidity of silicic acid increases more rapidly with increasing temperature than does that of other weak acids found in nature.

1908 **76** ALLEN, E. T., AND CLEMENT, J. K.: The Rôle of Water in Tremolite and Certain Other Minerals, *Am. J. Sci.*, [4] **26**, 101–18; *Z. anorg. Chem.*, **68**, 317–37.—A study of the loss of H_2O from various *hornblendes*. *Tremolite* which had been heated to 923° and had lost 85.1% of its H_2O was soaked in H_2O for 20 hours and dried at 110°; 11.8% of its H_2O was regained. A specimen of *tremolite* which had been heated to 933° and had lost 47.4% of its H_2O was heated with H_2O in a closed bomb at 400°, dried at 110°, contained 2.15% H_2O while the original mineral contained 2.31%. A *beryl* from which the H_2O has been removed by heating took up practically no H_2O when similarly treated.

1909 **77** FRIEDEL AND GRANDJEAN: Synthèse de chlorites par action des solutions alcalines sur le pyroxene, *Bull. soc. min.*, **32**, 150–4. Finely pulverized *augite* from a basalt heated at 450–460° showed little action; heated at 550–560° for 40 hours with a solution containing 4% Al_2O_3 and 5% NaOH gave (1) long feathers of **natrolite,** grouped in rosettes, identified by optical properties which are not given, (2) a few yellowish isotropic, very high index octahedra, probably **spinel,** (3) brilliant green micaceous plates, almost hexagonal, outline flattened perpendicular to the axis with smaller index, *i.e.*, the sharp negative bisectrix, negative, angle of optic axes small, variable, distinct pleochroism, X colorless or pale yellow, Y and Z green, crystals easily attacked by boiling HCl, probably a **chlorite,** (4) numerous small **indeterminable crystals.**

In the second experiment *diopside* from Zillertal was treated with a strong NaOH solution, about 25%, heated 40 hours at 550–570°; the only determinable mineral was a **chlorite,** in brownish red lamellae. The plates were flexible without elasticity, largest 0.1 mm., and were partly single, partly imbricate, partly irregularly ramified. Density = 2.67–2.70, composition: SiO_2, 28.4%; MgO, 36.2%; Al_2O_3, 15.2%; Fe_2O_3, 4.4%; CaO, 2.3%; H_2O, 11.5%; alkalies not determined. Outline hexagonal, but angles not 120°, biaxial, positive, larger index perpendicular to cleavage, optic angle small and variable, variations (with D-line) from 10–35° in the same crystal; $\gamma - \alpha = 0.0009$, dispersion large, strong pleochroism, Z brown, Y and X green or yellowish green, maximum absorption parallel Z. Similar in most respects to **penninite,** but direction of maximum absorption not the same.

1911 **78** BAUR, EMIL: Ueber hydrothermale Silikate, *Zeit. anorg. Chem.*, **72**, 119–61. Worked in a steel bomb, closed by a steel plug, and made tight by a copper washer. Preliminary experiments showed that the products obtained were substantially the same at 350° and 450°, and were independent of the amounts of H_2O; most of the experiments were made at 450°. No analyses were made of the products obtained, but analyses are given of the materials used. The data are summarized in the following table, the weights being given in grams. The asterisks refer to the crystallographic descriptions by Becke below:

No.	SiO_2	Al_2O_3	K_2O	H_2O	Misc.	Product
2, 7, 10	0.7	0.54	0.69	1.7	—	Orthoclase, kaliophilite, K faujasite [1]
31, 11	0.7	0.54	0.69	4.1	—	*Orthoclase, kaliophilite, K faujasite [1]
8, 9	0.7	0.29	0.37	1.6	—	Orthoclase, K faujasite [1]
12	0.7	0.21	0.26	3.0	—	Orthoclase, K faujasite [1]
32	0.7	0.12	0.16	1.8	—	Quartz, K faujasite [1]
41	0.7	0.54	0.69	2.1	0.5 CaO	Kaliophilite
44	0.7	0.37	0.48	4.0	0.1 $CaCO_3$	Kaliophilite, pectolite, orthoclase
56	0.6	0.29	0.55	6.0	0.21 CaO	*Kaliophilite, *K pectolite
57	1.44	0.21	0.96	6.0	1.0 $CaCO_3$	Orthoclase, calcite
58	1.44	0.21	0.96	6.0	2.0 $KHCO_3$ 1.0 $CaCO_3$	Calcite, gyrolite
59	1.44	0.41	1.23	6.0	2.0 $KHCO_3$ 1.0 $CaCO_3$	Orthoclase, calcite —
60	1.44	0.65	1.55	6.1	2.0 $KHCO_3$ 1.0 $CaCO_3$	Orthoclase, kaliophilite, calcite
65	0.7	0.71	0.26	3.3	—	*Andalusite, pyrophyllite
66	0.7	0.79	0.37	3.3	—	K faujasite,[1] pyrophyllite
67	0.7	0.60	0.37	3.2	—	Orthoclase, K faujasite,[1] pyrophyllite
68	0.7	0.87	0.48	4.3	—	Pyrophyllite
69	0.7	1.00	0.63	4.3	—	*Muscovite, K faujasite,[1] pyrophyllite
70	0.7	1.11	0.80	4.4	—	Kaliophilite, K faujasite[1]
72	0.95	1.14	0.63	4.5	0.17 CaO	Pyrophyllite, K faujasite,[1] kaliophilite
73	0.95	0.70	0.37	3.9	0.21 CaO	Pyrophyllite, orthoclase

(*Table continued on next page*)

No.	SiO_2	Al_2O_3	K_2O	H_2O	Misc.	Product
74	0.90	0.40	0.26 Na_2O	3.2	0.17 CaO	Opal, orthoclase
45	1.94	0.16	0.5	4.5	1.26 CaO	Pectolite
46	2.73	0.12	0.8	7.2	0.9 CaO	Pectolite, oligoclase
48	3.0	0.27	0.8	8.6	0.38 CaO	Pectolite, *quartz
49	1.8	0.09	0.64	5.5	1.0 $CaCO_3$	Pectolite, quartz
50	2.1	0.09	0.64	5.5	0.7 CaO	Pectolite, *oligoclase
51	2.1	0.09	0.64	5.5	1.2 $CaCO_3$	Pectolite, quartz, *gyrolite
52	2.1	0.22	0.72	5.6	1.2 $CaCO_3$	Pectolite, oligoclase
53	0.75	0.18	0.23	7.1	0.12 CaO	Pectolite, *stilbite
54	1.8	0.27	0.59	5.8	0.35 CaO 2.0 $CaCl_2$	Pectolite, oligoclase
55	1.8	0.3	0.77	5.6	1.1 $CaCl_2$	Pectolite, oligoclase
63	1.8	—	0.59	0.54	1.0 $CaCO_3$	*Pectolite, quartz
64	0.3	0.18	0.41	6.2	1.7 $NaHCO_3$	Amorphous
75	0.7	0.13	0.08	3.1	—	Quartz, albite
77	0.7	0.22	0.14	3.1	—	*Albite
78	0.7	0.31	0.19	4.2	—	Albite
79	0.7	0.81	0.19	4.5	—	Analcite
80	0.7	0.53	0.06	3.3	—	Opal, pyrophyllite
81	0.7	0.62	0.11	3.8	—	Opal, pyrophyllite
82	0.7	0.35	0.09	3.7	—	Opal
83	0.7	0.49	0.15	3.8	—	Opal
84	0.7	0.67	0.25	4.4	—	Amorphous

[1] Later identified as hieratite.

Optical determinations by Becke:

No. 48. **Quartz** with positive and negative rhombohedra; uniaxial, positive, ϵ–ω 0.009, refractive index that of α-quartz.

No. 31. **Orthoclase,** biaxial, ordinarily with rhomboidal outline, α in the short, γ in the long diagonal of the rhombus, extinction on the symmetry plane = 4–5°, γ = 1.524, α = 1.517.

No. 50. **Oligoclase,** refractive index of Canada balsam, 2 inclination angles = 63 and 72.5°, (100), (10$\bar{2}$), (101), extinction of α with trace of (001) = + 11°, α = 1.529, oligoclase-albite.

No. 77. **Albite,** angle (010) $\wedge$ (001) = about 64°, extinction of α = 20° with trace of (001).

No. 13. **K faujasite,** octahedra, n = 1.394, optically normal. (Later identified as hieratite, K_2SiF_6. See (85).)

No. 56. **Kaliophilite,** uniaxial, negative, birefringence about 0.005, ω = 1.525(6).

No. 65. **Andalusite,** columns, with parallel extinction, low terminations, angle of edge with vertical axis = 50°, γ or β 1.652.

No. 69. **Muscovite,** hexagonal tablets, with angles about 60°, extinction parallel to a pair of sides (β), β and γ in plane (001). β = 1.630. **Pyrophyllite,** rosettes and bundles, parallel extinction, γ in long direction, fairly high birefringence, $\gamma - \alpha$ = 0.002, refractive index = 1.50.

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No. 53. **Stilbite,** needles, α in direction of elongation, birefringence greater than 0.02, refractive indices larger and smaller than 1.495, α = about 1.488, plane of optic axes parallel to elongation, identification not certain.

No. 51. **Gyrolite,** hexagonal tablets, high birefringence, $\omega - \epsilon = 0.06$, $\omega = 1.529(?)$, identification not certain.

No. 63. **Pectolite,** needles with parallel extinction, γ in direction of elongation, birefringence = about 0.03, $\gamma = 1.620$.

No. 56. **K pectolite,** optically exactly the same as No. 63.

1912 **79** MÜLLER, W. J., AND KÖNIGSBERGER, J.: Über die Bildung von Silicatmineralien aus wässeriger Lösung bei höherer Temperatur, *Zeit. angew. Chem.*, **25**, 1273–7. A general account of the experiments described in (75), together with incomplete accounts of some new experiments. $KAlO_2$ or $Al(OH)_3$ with K water glass in proportions of $KAlSi_3O_8$ at 360–400° gave **Kanalcite** (?) or **leucite** (?); in the presence of CO_2 **orthoclase** with Baveno twinning was found. When, by the aid of a special apparatus, Na_2CO_3 was added to the filtered solution **orthoclase** was produced. Carbonates, therefore, precipitate orthoclase.

1912 **80** DOELTER, C., AND DITTLER, E.: Über einige Mineralsynthesen, *Sitzungsber. kaiserl. Akad. Wiss. Wien*, **121**, *Abt. I*, Oct., 1912, 897–914. 2.7 grams of $MgCO_3$ containing $Mg(OH)_2$ and 4.88 grams Na_2SiO_3 were moistened with H_2O and heated in a hard glass tube 100 hours at 200°, and the process several times repeated after washing the precipitate. (It is stated in a footnote that some work was done in an iron tube at 350°, but no indication is given as to what experiments or how many were so done.) The product was a mixture containing aggregates of needles, high birefringence, chief zone positive with extinction bisecting interfacial angles, refractive index = 1.588; the authors say that it was probably a silicate similar to **steatite.** **Magnesite** crystals were also present. A mixture of 3.08 g. mol $MgCl_2$ and 2.28 g. mol hydrated SiO_2 was fused at 1200° and H_2O vapor led over the product at 700–800°, but the product was not crystalline, and only 0.99% H_2O was taken up.

1912 **81** FENNER, C. N.: The Various Forms of Silica and their Mutual Relations, *J. Wash. Acad. Sci.*, **2**, 471–80. **Quartz** was easily prepared by heating either SiO_2 glass or precipitated SiO_2 in a steel bomb with Na_2CO_3 solution for 2–3 days at 400–500°. When either *tridymite* or *cristobalite* was treated similarly, **quartz** was always obtained. "In no case has the presence of tridymite or cristobalite in preparations made in aqueous solutions been detected, but, on the contrary, when the higher forms of SiO_2 have been used they have always recrystallized as **quartz.**"

1912 **82** FRIEDEL, G.: Synthèse de la néphéline potassique, *Bull. soc. min.*, **35**, 471–80.

Experimented with almost pure potassium *muscovite* and KOH to see whether the potassium homologue of nepheline could be prepared. 4 grams of finely divided potassium muscovite were treated with 22 to 25 cc. of a solution containing 0.177 g. of KOH per cc. in a copper lined steel tube at 510° to 600° C. for 40 to 45 hours. The copper was hardly attacked at 510°, but was vigorously attacked at 600°. The **copper** crystallized as cubes and octahedra on cooling; little, if any, remaining in solution. Similar phenomena may explain natural copper crystals; i.e., they may form from alkaline solutions.

The *muscovite* disappeared entirely with sufficient time and was replaced by short prisms and plates of **nepheline** (**kaliophilite**), with (0001) well developed. The crystals were rose-colored from included copper. There were also a few plates of **chlorite,** and rare needles of **natrolite.**

The nepheline was separated by means of a heavy liquid from all of the other material, except the included copper. Specific gravity = 2.65. Forms recognized were $(10\bar{1}0)$, (0001), and $(20\bar{2}1)$. $(0001) \wedge (20\bar{2}1) = 62°40' \pm 5'$. The parameters were those of natural nepheline, or of synthetic sodium nepheline, as closely as could be measured. Friedel determined a higher content of Fe_2O_3 than in natural nepheline or kaliophilite, but the similarity of properties indicated to him that the Fe_2O_3 is probably isomorphous with the Al_2O_3. Birefringence = .0051 ± .0002.

Duboin said that a mineral of the composition of potassium nepheline (kaliophilite) is formed from a melt in the presence of KF. He says that it is orthorhombic, biaxial, with a prism angle of 97°. Friedel found that it could also be prepared by hydrothermal methods, in which case it is like nepheline, or rather kaliophilite, with which it is probably identical. He postulated the isomorphism of the sodium and potassium forms.

1914 **83** MOREY, GEORGE W.: New crystalline silicates of potassium and sodium; their preparation and general properties, *J. Am. Chem. Soc.*, **36**, 215–30.

Crystalline silicates of potassium and sodium were prepared by heating glasses of different alkali : silica ratios in a bomb with water. In supplementary experiments the alkali was introduced as chloride, carbonate or hydroxide; the silica as silicate glass, quartz or amorphous precipitate. The result was always the same for the same alkali : silica ratio under the same physical conditions of the experiment. The products obtained were **hydrous glasses,** crystalline alkali silicates, or mixtures of the two. The equilibrium

details for the potassium system were worked out in a later paper (89) which see for a description of the compounds $KHSi_2O_5$ and $K_2Si_2O_5$ obtained in this study. In the sodium system **sodium disilicate,** $Na_2Si_2O_5$, prepared at 300°, commonly forms scaly crystals parallel to (010?). (110) ∧ (1̄10) = 31½°; (011) ∧ (01̄1) = 60°. 2E = 105°. Biaxial, negative. X = a; Y = b; Z = c. $\alpha = 1.504$; $\beta = 1.514$; $\gamma = 1.518$. Parallel extinction. **Sodium metasilicate,** Na_2SiO_3, prepared at 500°, forms poor acicular crystals with a cleavage parallel to the elongation. Parallel extinction; positive elongation. Probably uniaxial, positive. $\alpha = 1.513$; $\beta = 1.520$; $\gamma = 1.528$. 2V = 80°. (Indices and 2V by Morey and Bowen, 1926.)

1914 NIGGLI, PAUL: Einige vorläufige hydrothermale Synthesen, *Zeit.*
84 *anorg. Chem.*, **84**, 31–55.

Using a steel cylinder and silver crucible like the apparatus used by Baur (78), Niggli studied various mixtures of silica, alumina, ferric hydroxide, potash, and water. The volume of the bomb was between 18 and 19 cc. The runs were 1 to 2 days at 470° C. The materials were added as:

A—Amorphous silica with 2.48% alumina and 17.22% loss on heating.

B—Potassium aluminate with 33.35% Al_2O_3, 51.01% K_2O, and 15.69% loss on heating.

C—Ferric hydroxide with 75% Fe_2O_3 and 25% H_2O.

D—Aluminum hydroxide with 64.2% Al_2O_3 and 35.8% H_2O.

E—Potassium silicate with 34.17% SiO_2, 52.12% K_2O, and 13.71% loss on ignition.

The following table gives the weights in grams of these materials, and water, that were used in the different runs; also the approximate mol per cents of silica, alumina, ferric oxide, and potash for each run, and the products that were formed:

Exp. No.	Material added as: *A*	*B*	*C*	*D*	*E*	H_2O	Approximate mol %: SiO_2	Al_2O_3	Fe_2O_3	K_2O	Products
11	.50	.26	.20	—	—	6	66	10	9	14	Hematite, K aegirine, orthoclase
14	.34	—	.15	.23	.14	7	65	18	8	9	Hematite, kaliophilite, orthoclase
23	.49	.51	—	—	—	4	59	16	—	25	Orthoclase, kaliophilite
8	.74	.40	.70	—	—	5	59	8	19	14	Hematite, K aegirine, orthoclase, kaliophilite
21	.22	.20	.10	—	—	5	57	13	9	21	Hematite, K aegirine, kaliophilite, globulites (?)
15	.21	—	.12	.20	—	6	57	20	8	15	Hematite, orthoclase, globulites

(*Table continued on next page*)

Exp. No.	Material added as: A	B	C	D	E	H_2O	Approximate mol %: SiO_2	Al_2O_3	Fe_2O_3	K_2O	Products
10	.51	.41	.28	.08	—	5½	55	16	11	18	Hematite, kaliophilite, K aegirine, orthoclase
9	.48	.48	.29	—	—	7	53	14	11	22	Hematite, K aegirine, globulites, kaliophilite
6	.45	.48	.27	—	—	6	53	14	10	23	Hematite, K aegirine, globulites, kaliophilite
19	.39	.42	—	.18	—	6	52	26	—	22	Orthoclase, kaliophilite
27	.40	.36	.14	.22	—	5	50	25	6	19	Hematite, kaliophilite, poor globulites
12	.13	—	.10	.20	.22	6	50	21	8	21	Hematite, orthoclase, kaliophilite
22	.32	.60	—	—	—	4	44	22	—	34	Orthoclase, kaliophilite
18	.32	.37	.06	.34	—	6	43	34	3	20	Hematite, orthoclase, kaliophilite (pyrophyllite or kaolinite?)
26	.35	.67	.13	—	—	5	42	20	6	32	Hematite, orthoclase, kaliophilite
16	.32	.44	.17	.26	—	6	41	29	7	23	Hematite, orthoclase, ?
16	—	—	.11	.22	.84	6	32	9	4	55	No crystals; green mass

Descriptions of the minerals formed:

1. **Hematite:** Six sided, dark brown plates with very high index.

2. **Potassium aegirine:** Very thin, long prisms and needles with sharp terminations. The largest crystals were about .38 mm. long, .06 mm. wide, and .003 mm. thick. Higher birefringence in the centers indicated combinations of prisms and pinacoids. β slightly greater than 1.80; α lower than 1.80. Biaxial negative, large axial angle. Parallel extinction, with α parallel to the length. Light gold green, slightly pleochroic, with X somewhat more absorbed than Y. Birefringence = .02–.03. Insoluble in HCl.

3. **Orthoclase:** $n = 1.520 \pm$; characteristic twinning.

4. **Kaliophilite:** Six-sided plates; weakly birefringent; uniaxial negative; $n = 1.525$; soluble in HCl.

Niggli assigned the formula $KFeSi_2O_6$ to the potassium aegirine and considered that it was a connecting link between leucite and the amphibole-pyroxene group of the general formula $R'R'''Si_2O_6$. However, the material was too fine grained for separation and analysis, so it may contain considerable aluminum. He correlated the formation of the potassium aegirine with high iron content, high potash, but low alumina, although the table shows just as good correlation with the Fe_2O_3 content alone, all of the mixtures with 9 mol per cent or more of Fe_2O_3 yielding the mineral and none below that per cent yielding it.

Niggli suggested two reasons why potassium aegirine is not found in nature: (1) The absence of magmas that are rich in K_2O

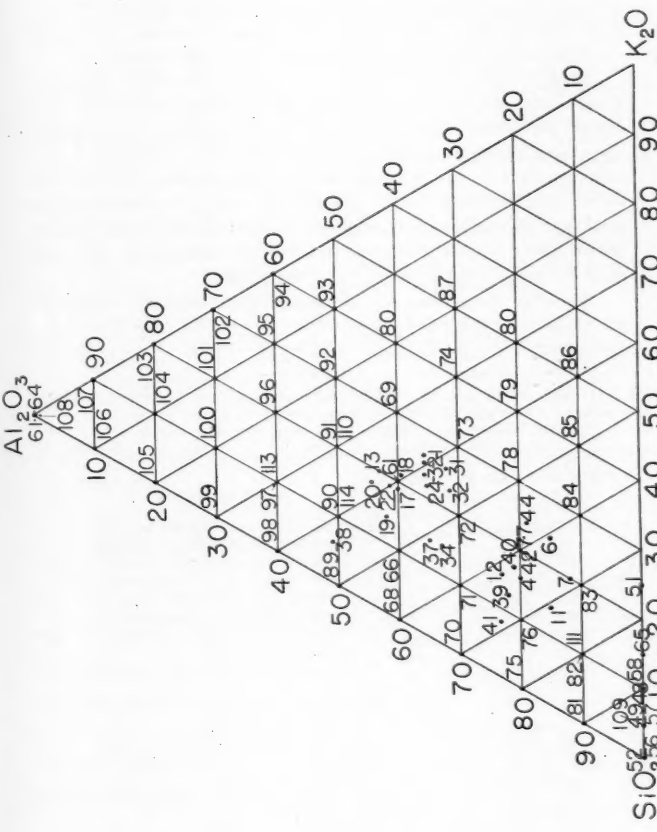

FIG. 6. Compositions of mixtures studied by Schlaepfer and Niggli (85) in the system $H_2O-K_2O-Al_2O_3-SiO_2$. See Table I for the details of these experiments.

and Fe_2O_3 but poor in RO, and (2) the greater affinity of K_2O for MgO, to form biotite, than for Fe_2O_3, to form potassium aegirine. He concluded that the formation of hematite in feldspars and the formation of analcite, zeolites, and sericite in igneous rocks may be brought about by hydrothermal activity during cooling.

1914 **85** SCHLAEPFER, M., AND NIGGLI, P.: Neue Beiträge zur hydrothermalen Silikatbildung, *Zeit. anorg. Chem.*, **87**, 52–80.

Using a steel bomb of 20 cc. volume much like the ones used in Baur's and Niggli's earlier work (**78** and **84**), Schlaepfer and Niggli performed a large number of hydrothermal experiments. The materials were placed in a silver crucible and heated 1 to 2 days at 470° C. In the majority of the experiments 2 cc. of water were used, but the amounts varied from 1 to 7 cc. The materials used may be summarized as follows for convenience in making the tables; for a complete list of the different samples of the same material and analyses, see p. 53 of the original:

A—amorphous silica; *C*—potassium aluminate; *D*—aluminum hydroxide; *F*—potassium hydroxide; *G*—K_2CO_3; *H*—CaO; *J*—ferric hydroxide; *K*—iron; *L*—$CaCl_2$; *M*—$FeCl_3$.

TABLE I (II AND III OF THE ORIGINAL)—MIXTURES IN THE SYSTEM K_2O-Al_2O_3-SiO_2-H_2O. Compositions of the mixtures are shown in mol per cents of potash, alumina, and silica in the ternary diagram, Fig. 6.

Exp. No.	Materials used in g. *A*	*C*	*D*	*F*	H_2O cc.	Products; remarks
4	0.70	0.54	0.19		3	Kaliophilite and amorphous material
6	0.70	0.70			7	Kaliophilite and amorphous material
7	0.80	0.60			7	Kaliophilite and amorphous material
11	1.00	0.50	0.20		2	Kaliophilite and amorphous material
12	1.00	0.60	0.50		7	Kaliophilite and amorphous material
13	1.00	1.40	1.80		5	Corundum and amorphous material
14	1.00	1.40	1.80		1	Corundum, kaliophilite, orthoclase, and amorphous material
15	0.50	0.70	0.90		5	Corundum, orthoclase, and amorphous material
17	0.80	0.70	0.90		5	Kaliophilite, corundum, pyrophyllite, and amorphous material
18	0.60	0.80	0.90		5	Corundum and amorphous material
19	0.60	0.50	1.00		5	Kaliophilite, pyrophyllite, amorphous material
20	0.50	0.60	1.00		5	Kaliophilite, corundum, amorphous material
21	0.70	1.20	0.80		5	Amorphous
22	0.70	1.10	0.80		2	Amorphous
23	0.70	1.00	0.80		2	Corundum, amorphous material (Temperature = 535°C)
24	0.70	0.90	0.80		2	Kaliophilite, pyrophyllite (?), amorphous
25	0.70	1.00	0.80		2	Amorphous
26	0.70	1.00	0.80		2	Corundum and amorphous material
27	0.60	0.70	0.90		5	Amorphous (Temperature = 330° C)

(*Table continued on next page*)

TABLE I (*Continued*).

Exp. No.	Materials used in g. *A*	*C*	*D*	*F*	H_2O cc.	Products; remarks
28	0.70	1.10	0.70		2	Amorphous
29	0.60	0.52*G*	1.25		2	Kaliophilite, corundum, amorphous material
30	0.60		1.25	0.424	3	Kaliophilite, corundum, amorphous material
31	0.70	1.10	0.60		2	Amorphous
32	0.70	0.90	0.60		3	Kaliophilite and amorphous material
34	0.80		1.10	0.31	3	Kaliophilite, orthoclase, amorphous material
35	0.80		1.10	0.38*G*	3	Kaliophilite and amorphous material
37	0.72		1.10	0.31	3	Kaliophilite and amorphous material
38	0.50		1.30	0.12	3	Amorphous
39	1.10		0.80	0.35	3	Kaliophilite (poor crystals), amorphous material
40	1.10		0.80	0.49	3	Kaliophilite and amorphous material
41	1.10		0.80	0.21	3	Amorphous
42	1.10		0.80	0.61	3	Kaliophilite and amorphous material
44	1.10		0.80	0.77	3	Kaliophilite and amorphous material
48	1.00			0.18	2	Glassy mass with small quartz crystals
109	1.30			0.105	2	Poorly crystallized quartz
52	1.37				2	Tridymite
56	1.37				2	Quartz and tridymite
49	1.30			0.105	2	Quartz and (hieratite)[1]
57	1.301			0.126	2	Quartz and (hieratite)
58	1.232			0.252	2	Quartz and (hieratite)
65	1.165			0.378	2	Small quartz crystals in glass
51	1.028			0.628	2	Amorphous glassy mass
81	1.232		0.317		2	Amorphous
82	1.098		0.317	0.251	2	Quartz, orthoclase (hieratite)
111	1.102		0.317	0.251	5	Quartz, orthoclase (poor crystals)
83	0.958		0.317	0.502	2	Poor crystals of orthoclase
84	0.822		0.317	0.753	2	Kaliophilite, unidentified silicate (No. 11)[2]
85	0.686		0.317	1.004	2	Kaliophilite
86	0.549		0.317	1.255	2	Poor crystals of kaliophilite
75	1.098		0.635		2	Amorphous
76	0.958		0.635	0.251	2	Orthoclase and opal (?)
77	0.822		0.635	0.502	2	Orthoclase, pyrophyllite(?), (hieratite)
78	0.686		0.635	0.753	2	Kaliophilite, orthoclase
79	0.549		0.635	1.004	2	Kaliophilite
80	0.411		0.635	1.255	2	Kaliophilite
70	0.958		0.951		2	Amorphous
71	0.822		0.951	0.251	2	Orthoclase and pyrophyllite(?)
72	0.686		0.951	0.502	2	Kaliophilite
73	0.549		0.951	0.753	2	Kaliophilite
74	0.411		0.951	1.004	2	Poor crystals of kaliophilite
87	0.275		0.951	1.255	2	Very poor microcrystalline kaliophilite
68	0.822		1.269		2	"Zunyite" and an aluminum silicate (No. 9)
66	0.686		1.268	0.251	2	Kaliophilite, pyrophyllite(?), Al silicate (No. 9)
67	0.549		1.269	0.502	2	Kaliophilite and amorphous material
69	0.411		1.269	0.753	2	Amorphous
88	0.275		1.269	1.004	2	Amorphous
89	0.686		1.586		2	"Zunyite" and aluminum silicate (No. 9)
90	0.549		1.586	0.251	2	Pyrophyllite(?) and amorphous material
114	0.551		1.586	0.251	5	Pyrophyllite(?) and amorphous material
91	0.411		1.586	0.502	2	Kaliophilite, bundle-like aggregates (No. 10)
110	0.413		1.586	0.502	5	Kaliophilite, bundle-like aggregates (No. 10)

(*Table continued on next page*)

TABLE I (*Continued*).

Exp. No.	Materials used in g. *A*	*C*	*D*	*F*	H_2O cc.	Products; remarks
92	0.275		1.586	0.753	2	Kaliophilite, bundle-like aggregates (No. 10)
93	0.137		1.586	1.004	2	Amorphous
98	0.551		1.904		2	"Zunyite" and aluminum silicate (No. 9)
97	0.411		1.904	0.251	2	Pyrophyllite(?) and amorphous material
113	0.412		1.904	0.251	5	Pyrophyllite(?)
96	0.275		1.904	0.502	2	Kaliophilite and aluminum silicate (No. 9)
95	0.137		1.904	0.753	2	Amorphous
94			1.904	1.004	2	Amorphous
99	0.412		2.221		2	"Zunyite" and aluminum silicate (No. 9)
100	0.275		2.221	0.251	2	Kaliophilite and aluminum silicate (No. 9)
101	0.137		2.221	0.502	2	Corundum and much amorphous material
102			2.221	0.502	2	Corundum
105	0.275		2.538		2	Aluminum silicate (No. 9)
104	0.137		2.538	0.251	2	Corundum and bundle-like aggregates (No. 10)
103			2.538	0.502	2	Corundum
106	0.137		2.855		2	Aluminum silicate (No. 9), amorphous material
107			2.855	0.251	2	Corundum
64 61			dried paste		3±	Corundum
108			3.175		2	Corundum

[1] Hieratite occurs in some of the experiments because part of the silica used contained fluorine as an impurity.

[2] The numbers in parentheses refer to the numbered descriptions of the minerals following the tables.

TABLE II (IV OF THE ORIGINAL)—MIXTURES IN THE SYSTEM SiO_2-Al_2O_3-K_2O-CaO-H_2O. 2 cc. of water used in each experiment and 0.112 g. of CaO, corresponding to 10 mol per cent. T = 470° C. Other values as shown in the table:

Exp. No.	Materials used; g. *A*	*D*	*F*	Mol per cents: SiO_2	Al_2O_3	K_2O	Products; remarks
115	1.237			90			Amorphous
116	1.099		0.251	80		10	Poorly formed quartz, amorphous material
117	0.962		0.502	70		20	Glassy
119	1.099	0.317		80	10		Amorphous
118	0.962	0.317	0.251	70	10	10	Orthoclase and amorphous material
120	0.824	0.317	0.502	60	10	20	Okenite(?) and amorphous material
121	0.687	0.317	0.753	50	10	30	Okenite(?) and amorphous material
122	0.550	0.317	1.004	40	10	40	Kaliophilite and amorphous material
123	0.962	0.635		70	20		Amorphous
124	0.824	0.635	0.251	60	20	10	Amorphous
125	0.687	0.635	0.502	50	20	20	Kaliophilite and amorphous material
126	0.550	0.635	0.753	40	20	30	Kaliophilite, unidentified needles (No. 14), and amorphous material
127	0.412	0.635	1.004	30	20	40	Kaliophilite, (calcite), amorphous
128	0.824	0.952		60	30		Amorphous
129	0.687	0.952	0.251	50	30	10	Amorphous
130	0.550	0.952	0.502	40	30	20	Kaliophilite and amorphous material

(*Table continued on next page*)

TABLE II (*Continued*).

Exp. No.	Materials used; g. *A*	*D*	*F*	Mol per cents: SiO_2	Al_2O_3	K_2O	Products; remarks
131	0.412	0.952	0.753	30	30	30	Kaliophilite, (calcite), amorphous
132	0.275	0.952	1.004	20	30	40	(Calcite) and amorphous material
133	0.687	1.269		50	40		Amorphous
135	0.550	1.269	0.251	40	40	10	Kaliophilite, pyrophyllite(?), amorphous
137	0.412	1.269	0.501	30	40	20	Kaliophilite and amorphous material
138	0.275	1.269	0.753	20	40	30	Kaliophilite, (calcite), amorphous
134	0.550	1.586		40	50		Amorphous
139	0.412	1.586	0.251	30	50	10	Kaliophilite and amorphous material
140	0.275	1.586	0.502	20	50	20	Kaliophilite and amorphous material
141	0.137	1.586	0.753	10	50	30	Amorphous
142	0.412	1.904		30	60		Amorphous
143	0.275	1.904	0.251	20	60	10	Kaliophilite, corundum, amorphous
144	0.137	1.904	0.503	10	60	20	Corundum and amorphous material
145*a*		1.904	0.753		60	30	Calcium aluminate (?-No. 13), amorphous
145*b*		1.904	0.753		60	30	Calcium aluminate (?-No. 13), amorphous
146	0.275	2.221		20	70		Amorphous
147	0.137	2.221	0.251	10	70	10	Corundum and amorphous material
148		2.221	0.502		70	20	Calcium aluminate (?-No. 13), amorphous
149	0.137	2.538		10	80		Amorphous
151		2.538	0.251		80	10	Amorphous
150		2.855			90		Corundum and amorphous material

Descriptions of the minerals and compounds in Tables I, II, and III:

I. Compounds in the system K_2O-Al_2O_3-SiO_2-H_2O:

1. **Alpha-quartz.** Hexagonal; uniaxial, positive; birefringence = .009. ϵ slightly above 1.55, but considerably below an oil of index 1.5692. Doubly terminated crystals with unequally developed rhombohedra are the commonest forms; faces identified are $(10\bar{1}0)$, $(10\bar{1}1)$, and $(01\bar{1}1)$. In Experiment 57, faces $(11\bar{2}1)$ and $(51\bar{6}1)$ were observed. Penetration twins are common and are of two kinds, with angles of 84° and 42° respectively.

2. **Tridymite.** Weakly birefringent hexagonal plates with the slow ray normal to the plates. $n = 1.476$. Penetration twins and spherical aggregates were also observed.

3. **Hieratite,** K_2SiF_6. This mineral was observed in violet-tinged isometric crystals showing combinations of octahedron, cube, and dodecahedron. $n = 1.33$–1.34. The necessary fluorine for its formation was contained in some of the silica samples, which were prepared from SiF_4. In some of the runs that contained aluminum a very similar mineral was obtained, with an index of about 1.39. Schlaepfer and Niggli believed this mineral to be identical with one prepared by W. Bruhns in 1889 (42) and also by

TABLE III (V OF THE ORIGINAL)—MIXTURES IN THE SYSTEM SiO_2-Al_2O_3-CaO-Fe_2O_3-H_2O.

Exp. No.	Materials used; amounts in grams: A	D	H	K	L	Mol per cents:[1] H_2O	SiO_2	Al_2O_3	CaO	Fe_2O_3	Products; remarks
53	.685		.560			2	50		50		Amorphous
54	1.028		.280			2	75		25		Amorphous
55	.548		.672			2	40		60		Amorphous
152	.687		.560		.400	3	50		50		Hillebrandite (21), monoclinic crystals (No. 17)
154	.687		.560		.050	3	50		50		Hillebrandite
155	.458		.746		.050	3	33		67		Monoclinic crystals (17), orthorhombic crystals (18)
175	.687		.560		.200	3	50		50		Hillebrandite
177	.687		.280	.300	.200	3	67		33	Fe	Augite, amorphous, FeCa-olivine
181			1.000	.500	.200	3			100	Fe	Calcium oxychloride (?-22), magnetite, amorphous[2]
185			1.000	.500		3			100		Calcium oxychloride
161	.687	.769	.280			3	50	25	25		Amorphous
153	.687	.769	.280		.409	3	50	25	25		Anorthite
158	.687	.769	.280		.050	3	50	25	25		Rare anorthite
160	.687	.769	.280		.200	3	50	25	25		Anorthite, rods (No. 23)
163	.687	.769	.280		.409	3	50	25	25		All amorphous
167	.687	.769	.280	.100*M*		3	50	25	25		All amorphous
168	.687	.769	.280	1.000[3]	.200	3	50	25	25	Fe	Magnetite, anorthite, CaFe-olivine
169	.687	.769	.280	.200	.200	3	50	25	25	Fe	CaFe-olivine, Fe oxide (29)
171	.687	.769	.280		.200	3	50	25	25		Amorphous
173	.687	.769	.280	.200	.200	3	50	25	25	Fe	Anorthite, CaFe-olivine
176	.687	.769	.280	.300	.200	3	50	25	25	Fe	Anorthite, CaFe-olivine
187	.687	.769	.280		.200	5	50	25	25		Amorphous
156	.887	.769	.280		.050	3	56	22	22		Scapolite (?-19), needles (20)
164	.824	.615	.224		.200	3	60	20	20		Anorthite
179[4]	.962	.362	.168	.300	.200	3	70	15	15	Fe	Anorthite, CaFe-olivine
186[4]	.962	.462	.168		.200	3	70	15	15		Anorthite
157	.590	.440	.479		.050	3	43	14	43		Anorthite, needles (No. 22)
159	.590	.440	.479		.400	3	43	14	43		Anorthite
182[4]	.590	.440	.479		.200	5	43	14	43		Anorthite
180*a*	1.000		.100*M*	.500		3	100			Fe	Fayalite
180*b*	1.000		.100*M*	.500		3	100			Fe	Fayalite
174	.687	.385	.280	.516*J*	.200	3	50	12.5	25	12.5	Babingtonite (?-No. 25)
172*a*	.687		.280	1.032*J*	.200	3	50		25	25	Babingtonite (?-No. 25)
178	.618		.336	.206*J*	.100	3	56		38	6	Needles (22), isotropic crystals (30)
172	.687		.280	.032*J*	.200	3	50		25	25	Babingtonite (?-No. 25)

[1] Mol per cents calculated neglecting $CaCl_2$, $FeCl_3$, and Fe.
[2] All of the rest of the runs in this series contained amorphous material.
[3] In a separate silver crucible.
[4] Heated 3 to 4 days instead of the 1 to 2 days of the other experiments.

174	.687	.385	.280	.516J	.200	3	50	12.5	25	12.5	Babingtonite (?-No. 25)
172a	.687		.280	1.032J	.200	3	50		25	25	Babingtonite (?-No. 25)
178	.618		.336	.206J	.100	3	56		38	6	Needles (22), isotropic crystals (30)
172	.687		.280	.032J	.200	3	50		25	25	Babingtonite (?-No. 25)

[1] Mol per cents calculated neglecting $CaCl_2$, FeCl₃, and Fe.
[2] All of the rest of the runs in this series contained amorphous material.
[3] In a separate silver crucible.
[4] Heated 3 to 4 days instead of the 1 to 2 days of the other experiments.

Emil Baur in 1911 (78), and identified by Becke as potassium faujasite. They suggested, therefore, that potassium faujasite should be taken from the list of minerals that have been prepared hydrothermally.

4. **Corundum.** Hexagonal plates or short prisms; uniaxial negative; birefringence is about .009; the mean index is approximately 1.76. Insoluble in HCl. No loss on heating. Some fan-shaped intergrowths were observed.

5. **Orthoclase.** Characteristic forms of orthoclase that has been prepared hydrothermally. See (84).

6. **Kaliophilite,** $KAlSiO_4(+ H_2O?)$. This mineral is called potassium nepheline in the original paper. It is identical with the mineral called potassium nepheline hydrate by Baur (78) and by Niggli (84). Schlaepfer and Niggli concluded that the water (less than 1.5%) had no significant rôle, since the index, 1.525, is relatively high, and that there was nothing in their provisional identification that conflicted with its identity with kaliophilite. It was observed commonly in hexagonal plates or little prisms, but in two experiments, 79 and 84, it occurred with pyramids.

7. **Pyrophyllite** (?), $HAlSiO_4$. Small plates commonly as sheaf- or rosette-like aggregates. Parallel extinction; positive elongation; high birefringence. $n = 1.58 +$.

8. **Zunyite-like mineral.** Isometric tetrahedra sometimes showing small faces of negative tetrahedra and cubes. $n = 1.545$–1.547. Insoluble in HCl.

9. Orthorhombic (?) **aluminum silicate.** These crystals were found in potash-free charges with a high content of alumina. They showed parallel extinction and positive elongation. $\gamma = 1.6229$. The crystals had sillimanite-like forms, but the index and birefringence were too low for either natural or artificial sillimanite.

10. Small **bundle-like aggregates** of scales with parallel (?) extinction and index about 1.657.

11. **Monoclinic needles** (Experiment 84). $\alpha \wedge$ length = 30–35°. $\gamma = 1.523 \pm$.

II. Compounds in the system SiO_2-Al_2O_3-K_2O-CaO-H_2O.

12. **Okenite** (?), $CaSi_2O_5 \cdot 2H_2O$. Orthorhombic; frequently in tufts of crystals with positive elongation and index about 1.55. Weak birefringence; decomposed by HCl.

13. **Calcium aluminate** (?). Broad prisms and needles that commonly have dome-like terminations. Parallel extinction with γ parallel to the length. Lowest index about 1.625. Penetration twins. These properties do not agree with those of any of the calcium aluminates prepared by Shepherd and Rankin.

14. Fine **undetermined needles** with a mean index of about 1.62.

15. **Calcite.** Rhombohedral; ϵ' parallel to the short diagonal. Very high birefringence; $\omega = 1.657$. The carbon dioxide probably came from impurities in some of the KOH.

III. Compounds from CaO, SiO_2, Al_2O_3, and H_2O, with the addition of chlorides to some of the mixtures.

16. **Anorthite.** Triclinic tablets with the habit and properties of anorthite.

17. Small rod-like monoclinic crystals with $\gamma \wedge$ length = 7°. Highest index = 1.657 +; slight birefringence. Soluble in HCl. Penetration twinning. Supposed to be an **amphibole-like form of $CaSiO_3$**, because the conditions of the experiment limit it to containing SiO_2, CaO, H_2O, and HCl.

18. Weakly birefringent crystals with orthorhombic form. Index, about 1.64. Soluble in dilute HCl. Perhaps an **orthosilicate of calcium.**

19. **Scapolite-like mineral.** Tetragonal; uniaxial, negative; very blunt double pyramids. Higher index = 1.52; birefringence = .01 +. Difficultly soluble, or insoluble, in cold concentrated HCl. Perhaps a meionite with some water and chlorine in the molecule, since CaO, Al_2O_3, SiO_2, H_2O, and Cl^- are the possible components.

20. **Needle-like orthorhombic (?) crystals.** Positive elongation. Mean index = 1.67–1.68; birefringence not high. Very difficultly soluble, or insoluble in cold HCl.

21. **Hillebrandite,** $Ca_2SiO_4 \cdot H_2O$. Orthorhombic; positively elongated needles with parallel extinction. Highest index is 1.61–1.63; birefringence slight. Soluble in HCl. These crystals were reported from charges containing CaO, $CaCl_2$, SiO_2, and H_2O.

22. **Calcium oxychloride** (or hydrate?). Positively elongated needles with parallel extinction. Indices, 1.59–1.61; slight birefringence. Soluble in HCl. Experiment 181.

23. Small **rod-like crystals** with dome terminations. $n = 1.523$; birefringence not perceptible even with the sensitive tint. Decomposed by cold HCl.

24. **Hedenbergitic augite.** Monoclinic, fibrous crystals; $Z \wedge c$ = 46–47°. Birefringence is of the order of magnitude of .03. Crystals showing inclined extinction and high birefringence when turned 90° about the long axis show bilateral symmetry and much lower birefringence, with β normal to the symmetry plane. This demonstrates that they are monoclinic. Index is about 1.76; the crystals are light yellow green in color. Insoluble in HCl.

25. **Babingtonite-like mineral.** Triclinic (?); poorly formed needle-like crystals. In sections of relatively high birefringence X or $Y \wedge$ elongation = 22–25°. These sections clearly show

dichroism, with X′ = green, Y′ = dirty brown-green. Indices, 1.715–1.76. Insoluble in HCl.

26. **Iron calcium olivine,** $(Fe, Ca)_2SiO_4$. Short prismatic orthorhombic crystals with pyramidal terminations. Crystals may show either positive or negative elongation. Sections showing positive elongation have stronger birefringence, .030–.035, than those showing negative elongation, .005–.010. Small axial angle. Indices probably between 1.8 and 1.9. Biaxial negative. Light yellow. Easily decomposed by HCl.

27. **Fayalite,** Fe_2SiO_4. Runs with iron, ferric chloride, and silica produced wedge-shaped orthorhombic crystals of fayalite. Parallel extinction; positive or negative elongation. Indices between 1.8 and 1.9. The crystal faces were not as well developed as were those of No. 26; higher birefringence than No. 26, about .040.

28. **Magnetite.** Small octahedra with characteristic blue-black color under the microscope. The crystals occurred on the surface of the iron wire in Experiment 168, where the wire was in a separate silver crucible.

29. Unknown **iron oxide.** Orthorhombic; small honey-yellow crystals with parallel extinction, Z parallel to *c*. Pleochroic, with the higher index yellow and the lower one brownish yellow. Indices considerably above 1.76. Easily soluble in HCl. At 300° C. the crystals change to a black granular substance with the bluish luster of magnetite. The same change takes place at ordinary temperatures in 2 to 3 days. The suggestion is made that this compound may be an unstable **chrysoberyl modification of Fe_3O_4; geothite** is regarded as less likely.

30. Small isometric crystals with index 1.76 from charges with CaO, Fe_2O_3, SiO_2, H_2O, and $FeCl_3$. Possibly an **iron calcium garnet.**

Listed as positively identified are: **quartz, tridymite, hieratite, corundum, orthoclase, calcite, kaliophilite, anorthite, hillebrandite, iron calcium olivine, fayalite,** and **magnetite;** as tentatively identified **zunyite, pyrophyllite, okenite,** a **scapolite, hedenbergitic augite, babingtonite,** an **orthorhombic modification of Fe_3O_4,** and a **calcium amphibole.** Photomicrographs of 18 of the minerals described are given.

They conclude that some minerals, such as **orthoclase, quartz, kaliophilite,** and **corundum,** occur again and again under hydrothermal conditions with certain concentrations at 470° C., but other minerals seem to require much more definite conditions. They discuss the physical chemistry of each system briefly, but too much in detail to be repeated here.

They call attention to the fact that many of the minerals that they have prepared at 470° in the presence of water are commonly formed in nature, and in the laboratory, from melts and at much higher temperatures; for example, **quartz, tridymite, anorthite,** and **fayalite.** They also mention that many of these minerals are found in pegmatites, while others, such as **okenite, hillebrandite, scapolite, calcium amphibole,** and **corundum,** are characteristic of contact deposits.

Typical zeolites do not appear in the products of any of the experiments and this is taken to indicate that they are the result of hydrothermal activity at lower temperatures. Epidote and zoisite, which were expected, did not appear in any of the experiments. A run of 14 days at 360° C. with a charge with molecular ratios as follows: $4CaO : 2Al_2O_3 : 1Fe_2O_3 : 6SiO_2$, with 4 grams of water, produced a **babingtonite-like** mineral with no trace of epidote or zoisite.

1915 **86** CHURIN, N.: Synthesis of apophyllite, *Bull. Acad. Sci. Petrograd,* **9**, 1913–18.

Because apophyllite often occurs in nature associated with calcite, it occurred to Churin that it might be synthesized from calcite. He mixed 2.5 g. of finely powered *calcite* with 7.5 g. of K_2SiO_3 and 22 cc. of water and heated the mixture in sealed glass tubes for 226 hours at 210° C., with water that had been saturated with CO_2.

Microscopical examination showed crystals with (100), (111), and (001) that were taken to be **apophyllite.** The crystals were uniaxial positive and intumesced before the blowpipe. Specific gravity = 2.384. Secondary reactions are assumed because the treated charges showed some **wollastonite,** unchanged (?) **calcite,** and amorphous (?) $CaCO_3$. Similar reactions probably take place in nature where aqueo-igneous solutions are rich in calcium and silica, or where siliceous solutions react with calcareous rocks.

1916 **87** SCHNEIDERHOHN, H.: Über die Umbildung von Tonerdesilikaten unter dem Einfluss von Salzlösungen bei Temperaturen bis 200°, *Neues Jahrb. Min. Geol.*, **BB 40**, 163–228.

A detailed summary of the work of Lemberg, (10), (26), (31), (40), (41), and of Thugutt, (54), (56). Included are also summaries of several other articles dealing with the constitution and use of some natural minerals, especially the zeolites.

1916 **88** STEPHENSON, E. A.: The action of certain alkaline solutions on feldspar and hornblende, *J. Geol.*, **24**, 180–99.

Copper tubes plugged with copper and sealed in the oxy-acetylene torch were used in the experiments. The copper was

unattacked by the solutions, except the sulfides, which produced some **chalcocite.**

N/2 $KHCO_3$ produced no change in *adularia*, *albite*, or *hornblende* after 15 days at 233° C. and 30 atmospheres pressure, or at 280° C. and 65 atmospheres.

N/4 $Na_2B_4O_7$ produced **analcite** from *adularia*, but produced no change in *albite* or *hornblende* in 15 days at 233° C. and 30 atmospheres.

N/2 Na_2S formed **analcite** and **needles** of another mineral from *adularia;* **analcite** alone was formed from *albite*, and no change was produced in *hornblende* in 15 days at 233° C. and 30 atmospheres.

A saturated solution of $Ca(HCO_3)_2$ produced no change in *albite* or *hornblende* in 16 days at 280° C. The pressure was probably about 65 atmospheres; the tubes burst.

N/2 $NaAlO_2$ produced **analcite** from *adularia* in 15 days at 280° C. and 65 atmospheres.

N/2 $KAlO_2$ produced **hexagonal plates** and **needle-like crystals** from *adularia* and *orthoclase*. **Hexagonal plates** were produced by the action of this solution on *albite*, but it produced no change in *hornblende*. These runs were for 15 days at 280° C. and 65 atmospheres.

Other results may be summarized in tabular form shown in the table on page 686.

The needles produced in Experiments 24, 25, 34, 35, and with Na_2S have an extinction direction forming an angle of less than 2° with the elongation; negative elongation; n, parallel to length, = 1.490 and, normal to elongation, = 1.517. After drying at 110° C. the crystals gave no water in the closed tube.

The elbow twins of Experiment 25 have an angle of 106° between individuals. The crystals are transparent and have an index slightly above 1.565. Extinction ∧ elongation = 43°. Probably monoclinic.

No kaolin-like substance was formed at temperatures up to 280° C. From this negative evidence Stephenson suggests that perhaps kaolin is formed by the action of acidic solutions. This is in agreement with the results of other workers.

1917 **89** MOREY, GEORGE W., AND FENNER, C. N.: The ternary system H_2O-K_2SiO_3-SiO_2, *J. Am. Chem. Soc.*, **39**, 1173–1229.

This is a continuation of Morey's earlier work (83), giving the equilibrium relations in a portion of the system H_2O-K_2O-SiO_2 from 200 to 1000° C. The following methods were used:

1. The isothermal polybaric saturation curves were determined by the hydrothermal-bomb quenching method. A given amount of a given *glass* was treated at a given temperature in a bomb and

Exp. No.	Mineral Used	Solution	Volume Solution	Volume Tube	T(°C.)	Pres. Atm.	Time	Results
1	Adularia	H_2O	300 cc.	100 cc.	100	1	14 da	No alkalinity
3	Adularia	"	50	80	183	11	82 da	No alkalinity
2	Hornblende	"	300		100	1	14 da	No alkalinity
4	Hornblende	"	50	80	183	11	82 da	No alkalinity
5	Adularia	N/2 Na_2CO_3	1000		15	1	3 yr 1 mo	No change
6	Adularia	"	300		100	1	90 da	No change
7	Adularia	"	50	80	183	11	82 da	Analcite
8	Adularia	"	40	85	233	30	18 da	Analcite
9	Microcline	"	40	85	233	30	18 da	Analcite
11	Hornblende	"	1200		15	1	3 yr 1 mo	No change
12	Hornblende	"	300		100	1	90 da	No change
13	Hornblende	"	60	85	183	11	82 da	No change
14	Adularia	N/10 KF	60	85	183	11	82 da	No change
15	Adularia	"	50	80	233	30	18 da	No change
16	Microcline	"	40	75	233	30	18 da	Minute rods
17	Albite	"	30	70	233	30	18 da	No change
18	Hornblende	"	60	85	183	11	18 da	Brown iron oxide
20	Adularia	N/2 Na_2CO_3 + N/10 KF	300		100	1	90 da	No change
21	Adularia	"	54	80	183	11	41 da	No change
22	Adularia	"	60	80	183	11	82 da	No change
23	Adularia	"	40	85	233	30	18 da	Analcite
24	Adularia	"	60	100	280	65	15 da	Needles
25	Orthoclase	"	50	100	280	65	15 da	Twinned crystals and needles
26	Microcline	"	48	100	233	30	18 da	No change
27	Albite	"	48	80	233	30	18 da	Analcite
28	Hornblende	"	300		100	1	90 da	No change
29	Hornblende	"	60	85	183	11	41 da	No change
30	Hornblende	"	60	85	183	11	82 da	No change
31	Hornblende	"	60	85	233	30	3 da	No change
32	Adularia	N/2 $NaHCO_3$	45	85	233	30	15 da	Analcite
33	Adularia	"	59	85	280	65	15 da	Analcite
34	Albite	"	45	85	233	30	15 da	Analcite and needles
35	Albite	"	60	105	280	65	15 da	Needles
36	Hornblende	"	45	85	233	30	15 da	No change
37	Hornblende	"	45	85	280	65	15 da	No change

quenched at such a rate that the water dissolved in the charge at the temperature and pressure of the run remained in it after quenching. The amount of water in the bomb was varied in different runs until the saturation point, i.e., the point at which the first crystals were found in the quenched charge, was determined. Such a series of experiments determined one point on a given isotherm. These isothermal saturation curves are shown below in Fig. 7.

The pressure was calculated as follows: the total amount of water in the bomb less the water taken up by the charge represented the amount of water that was in the vapor phase. From

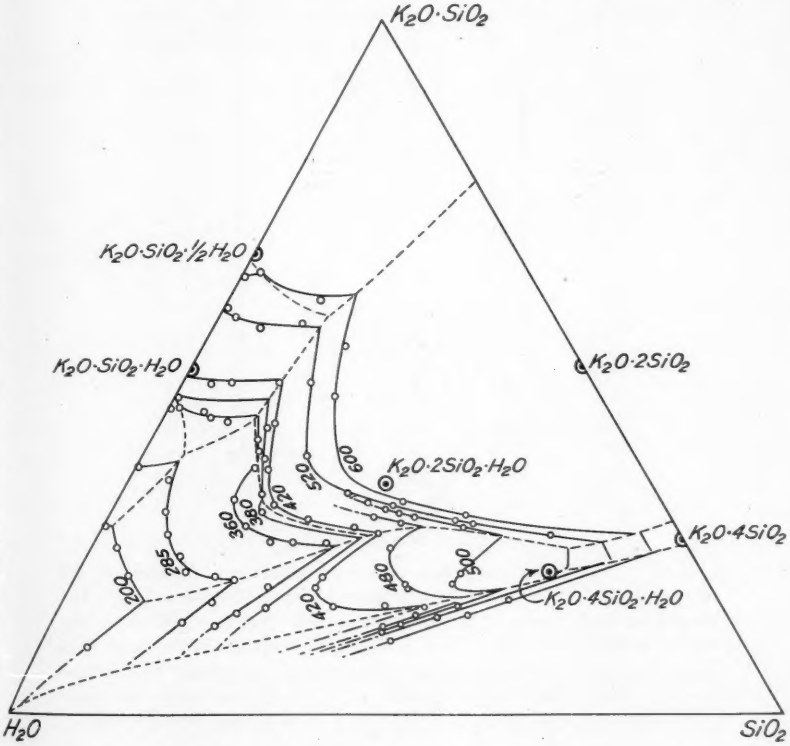

FIG. 7. Isothermal polybaric saturation curves in the system $H_2O - K_2O - SiO_2$. After Morey and Fenner (89).

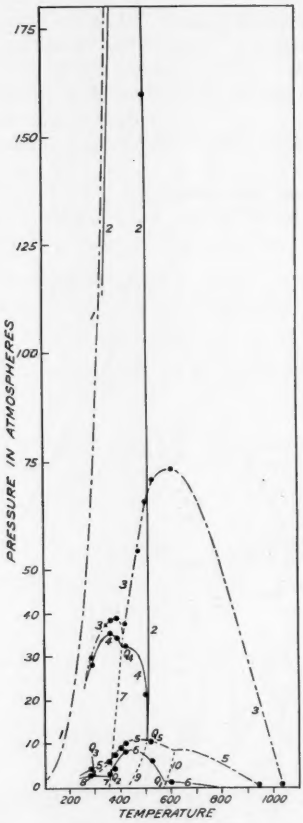

FIG. 8. Pressure-temperature curves of univariant equilibria in the ternary system $H_2O-K_2O-SiO_2$. After Morey and Fenner (89). The short-long dash curve, 1, is the vapor pressure curve of water; 3, the binary system $H_2O-K_2O\cdot 2SiO_2$; 5, the binary system $H_2O-K_2O\cdot SiO_2$. The full curve, 2, is the vapor pressure curve of the ternary equilibrium $V + L + K_2O\cdot 4SiO_2\cdot H_2O$ + quartz; 4, $V + L + K_2O\cdot 2SiO_2$ (or $K_2O\cdot 2SiO_2\cdot H_2O$) + $K_2O\cdot 4SiO_2\cdot H_2O$; 6, $V + L + K_2O\cdot SiO_2 + K_2O\cdot 2SiO_2$.

this value and the known volume of the bomb (70 cc.) and the temperature of a given run the pressure was calculated by means of Van der Waals' equation. The pressure-temperature curves are shown in Fig. 8.

2. The isobaric polythermal saturation curve at one atmosphere was determined by holding partly crystallized material in steam at one atmosphere long enough for equilibrium to be attained, then quenching. By varying the temperature, while keeping the composition and pressure constant, until the last crystals disappeared a point on the isobar was obtained. Other points were obtained by repeating this procedure for mixtures of different compositions. The other isobars were obtained from sections parallel to the base of the pressure-concentration diagram. These isobars are shown in Fig. 9.

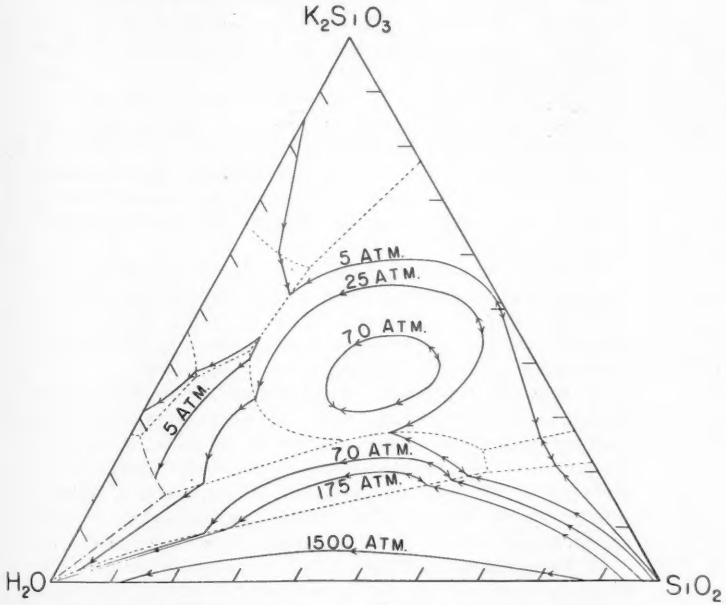

FIG. 9. Polythermal isobaric saturation curves in the ternary system $H_2O-K_2O-SiO_2$. After Morey and Fenner (89). These curves represent sections of the solid pressure-temperature-composition model, at several constant pressures, and with temperature falling in the directions indicated by the arrows.

3. Solubilities at different temperatures were determined by placing a small weighed amount of *glass* in a bomb with a given amount of water and heating to a given temperature. The amount of solid was varied until it just dissolved in the given amount of water. The solubilities of the five potassium silicates described are shown in Fig. 10. The curves obviously represent the solubility or melting point curves in the binary systems H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$.

Descriptions of compounds:

1. Silica. **Quartz** was obtained in these experiments from 200° to 600°. Traces of inversion could not be determined because of the smallness of the crystals.

2. **Potassium hydrogen disilicate,** $KHSi_2O_5$. Orthorhombic crystals, well developed; prismatic, with (100) and (001) prominent. (001) $\wedge$ (100) = 90°; (100) $\wedge$ (110) = 52° 32′; ($\bar{1}$10) $\wedge$ (110) = 74° 56′. Exceptionally the crystals are tabular parallel to (001) or (100). It has cleavages well developed parallel to (100) and (010). Biaxial, positive; X = *b*; Y = *c*; Z = *a*. α = 1.482, β = 1.489, γ = 1.530; 2E = 70–75°, 2V = 45–48° (subsequent unpublished determination by H. E. Merwin). Parallel extinction, axial plane parallel to elongation. D. = 2.417, decomposed by water below 420°, slowly at ordinary temperature; decomposed by dilute HCl leaving residue of birefringent SiO_2; congruent melting point ca. 515°. No loss of H_2O at 350°, but the loss becomes appreciable at 450°.

3. **Potassium disilicate,** $K_2Si_2O_5$. Orthorhombic, platy, showing 3 cleavages, the best of which is micaceous and normal to the acute negative bisectrix. α = 1.503, γ = 1.513, negative, 2V large (Kracek, Bowen and Morey, *J. Phys. Chem.*, **33**, 1857 (1929)). Melting point 1041°, decomposed by water below 200°.

4. **Potassium disilicate monohydrate,** $K_2Si_2O_5 \cdot H_2O$. This compound rarely forms large or well developed crystals; the ones that are formed are decomposed rapidly by water at ordinary temperatures. Decomposed by water below 280°; melts incongruently at 405° with the formation of vapor and a solution saturated with $K_2Si_2O_5$. The crystals are commonly rounded grains; biaxial, positive, small axial angle; high birefringence.

5. **Potassium metasilicate,** K_2SiO_3, is extremely deliquescent. It occurs usually in rounded grains without crystal boundaries. There is a fair cleavage that is parallel to γ, but the crystallographic relations of the cleavage are not known. The crystals are biaxial, positive, with high birefringence and strong dispersion, $v > \rho$. 2E = 78.5°. This compound is the stable solid phase in

FIG. 10 (left). Solubility or melting-point curves in the binary systems $H_2O-K_2SiO_3$ and $H_2O-K_2Si_2O_5$. The corresponding vapor pressures are given in Fig. 8. After Morey and Fenner (89).

FIG. 11 (right). The solubility of silica in water. After Lenher and Merrill (90), Gruner (112), and Hitchen (139).

the binary system H_2O-K_2SiO_3 from about 610° to its melting point at 996° C.

6. **Potassium metasilicate hemihydrate,** $K_2SiO_3 \cdot 0.5H_2O$, is the stable solid phase in the binary system from 370° to 610°. It occurs as well-formed, elongate crystals that are commonly terminated, with the interior terminal angle either about 70° or a little greater than 90°. The crystals show a cleavage parallel to the elongation, parallel extinction, and positive elongation. They are biaxial, probably positive, and have high birefringence. Completely soluble in water. Distinguishing features are the elongate crystal habit and the large axial angle.

7. **Potassium metasilicate monohydrate,** $K_2SiO_3 \cdot H_2O$, is decomposed by water below 200°, and melts incongruently at 370° into $K_2SiO_3 \cdot 0.5H_2O$, liquid, and vapor. The crystals are commonly equant grains; biaxial positive; high birefringence; small axial angle. They dissolve completely in water.

Potassium orthosilicate was not formed in mixtures ranging from $2K_2O : SiO_2$ to $K_2O : SiO_2$ in an atmosphere of steam up to 1100° C.

1917 **90** LENHER, V., AND MERRILL, H. B.: The solubility of silica, *J. Am. Chem. Soc.*, **39**, 2630–38.

Lenher and Merrill studied the solubility of various forms of silica in water and in solutions of HCl and H_2SO_4 at temperatures below 100° C. They found a definite, measurable solubility under these conditions, and that the magnitude of the solubility depends upon the temperature and concentration of the acid. They believed the solubility to be the same whether ignited or gelatinous silica was used, but were unable to prove that point, because equilibrium was never reached with the ignited silica in the time of the runs. Equilibrium was reached with gelatinous silica in less than 24 hours, and the solubility was independent of the method of preparation. Numerous graphs and tables give the quantitative results and show that the solubility increases with increasing temperature and decreases with increasing concentration of acid solutions. Very dilute acids dissolved .02 g. of silica per 50 cc. at 90° C., but the solubility decreased almost to zero for 50% acids. At 25° C. 3% HCl dissolved .007 g. per 50 cc. and 20 %HCl dissolved less than .001 g. per 50 cc. at the same temperature.

Pure water dissolved .0214 g. per 50 cc. at 90° and .0081 g. at 25°. For a comparison of these results with water with those of Hitchen and of Gruner see the graph of Fig. 11, p. 691.

1918 **91** KÖNIGSBERGER, J., AND MÜLLER, W. J.: Über hydrothermale Mineralbildung, *Zeit. anorg. Chem.* **104**, 1–26.

Working with a steel bomb (volume = 125 cc.) much like the

one used in earlier work (75), Königsberger and Müller continued their work on the hydrothermal formation of minerals. The bomb was lined with a platinum-iridium alloy and fitted with a platinum-iridium filter tube. The results of their experiments are summarized in the following paragraphs and the table on pp. 694–5:

Other experiments not tabulated; Group V, *labradorite* treated with alkali carbonates. The labradorite contained approximately 50% SiO_2, 20% Al_2O_3, 12% CaO, and 5% Na_2O, by weight. In each experiment the solution was filtered for 12 hours at the temperature of the run.

Experiment 62. 2 grams of *labradorite* in pieces of about one cubic millimeter were heated at 400° C. for 24 hours with 30 cc. of water, 1.2 g. of K_2CO_3, and 0.36 g. of NaCl. About two-thirds of the labradorite remained unchanged. Of the transformed part about .8 was **zeolite,** Z_1; .05, **kaliophilite;** .07,**orthoclase;** and .07, **pectolite.** In the filter tube there was a trace of the **zeolite.**

Experiment 64. The same mixture as in 62 was heated for 24 hours at 340°. About 1/20 of the *labradorite* was transformed. Of this part about .7 was **zeolite,** Z_1; .2, **calcite;** .1, **pectolite.**

Experiment 66. 10 grams of *labradorite* mixed with 1 g. of NaOH, .3 g. K_2CO_3, 1 g. of KCl, and 40 cc. of water were heated 96 hours at 330°, filtered and cooled for 36 hours. 1/6 of the *labradorite* was transformed: .2, **zeolite,** Z_2; .1, **pectolite;** .7, **nepheline.** There was a trace of **zeolite** in the filter tube.

Experiment 65. 5 grams of *labradorite* mixed with 1 g. of NaOH, 1 g. of KOH, .3 g. K_2CO_3, and 40 cc. of water. The mixture was heated for 76 hours at 330° and filtered 12 hours at the same temperature, then cooled during 36 hours. 1/20 of the *labradorite* was changed: .9, **nepheline;** .1, **pectolite.**

Group VI, Experiment 71. A mixture of *hematite* and *chlorite* was heated in 30 cc. of water for 48 hours at a temperature of 420° with 1.5 g. of Na_2O, 1 g. of K_2O, 2 g. of CO_2, and .5 g. Cl_2. The solution was filtered off at the same temperature and cooled during 24 hours. There was a slight formation of new **chlorite** on the pieces of hematite, which not noticeably dissolved. In the filter tube there was about .01 g. of brown colloidal hydrous **iron oxide** and a little chlorite powder, which was probably not a new formation.

Descriptions of the minerals prepared:

1. **Zeolites:**

Analcite in small trapezohedra with $n = 1.465–1.478$. Soluble in HCl, leaving skeletons of silica. The **analcite** never occurred in experiments where soda was absent, but probably contained some

Exp. No.	Time, Hrs.	Temp. °C.	H_2O cc.	Materials Used; Amounts in Grams K_2O	Al_2O_3	SiO_2	Na_2O	CO_2	Others	Mol Per Cents K_2O	Al_2O_3	SiO_2	Added as [1]	Products Bottom Mass	Filter Tube
60	24[4]	330	30	3.36	0.64	5.67				26	4.6	69.4	*BC*	Zeolite A, leucite, kaliophilite	
58	10	370	30	0.53	0.88	1.89				12	19	69	*BC*	Leucite, kaliophilite, pectolite, microlites	
57	24[2]	440	30	0.53	0.88	1.89				12	19	69	*AC*	Leucite, kaliophilite, orthoclase, pectolite, microlites	
B	10	410	30	0.74	0.80	1.98				16	16	68	*ACE*	Leucite, kaliophilite, orthoclase, amorphous material	
59	24[2]	320	30	6.58	0.64	5.67		0.64		37	4	59	*BEF*	Leucite, kaliophilite, calcite	Quartz, calcite
1	3	310	40	1.06	0.34	3.80		5.00		14.5	4.2	81.3	*ACG*	Zeolite A, leucite, amorph. material	
2	24[2]	310	40	1.06	0.34	3.80		5.00		14.5	4.2	81.3	*ACG*	Leucite, quartz, amorph. material	Quartz
3	24[2]	420–30	40	1.06	0.34	3.80		5.00		14.5	4.2	81.3	*ACG*	Leucite, orthoclase, micaceous zeolite, quartz, microlites	Quartz, microlites
A	24	360	40	1.06	0.34	3.80		2.00		14.5	4.2	81.3	*ACG*	Micaceous zeolite, microlites	
80	12	300	21	0.53	0.88	1.89	0.12	0.09		15	18	67	*BCI*	Analcite, nepheline	
61	60[4]	360	33	0.53	0.88	1.89	0.12	0.09		15	18	67	*BCI*	Nepheline, orthoclase, pectolite	
60*a*	24	365	33?	0.53	0.88	1.89	0.12	0.09		15	18	67	*BCI*	Nepheline, orthoclase	Orthoclase
56	14	350–60	33?	0.53	0.88	1.89	0.12	0.09		15	18	67	*ACI*	Leucite, nepheline, microlites	

Exp. No.	Time, Hrs.	Temp. °C.	H_2O cc.	Materials Used; Amounts in Grams K_2O	Al_2O_3	SiO_2	Na_2O	CO_2	Others	Mol Per Cents K_2O	Al_2O_3	SiO_2	Added as [1]	Products Bottom Mass	Filter Tube
68	12	340	30	3.36	0.64	5.67	0.30	0.20	.5 NaCl	29	4.5	66.5	*BCIJ*	Zeolite Y, leucite, nepheline, amorphous material	Zeolite Y
67	12[5]	340	30	3.36	0.64	5.67	0.30	0.20	.5 NaCl	29	4.5	66.5	*BCIJ*	Zeolite Y, nepheline pyrophyllite, amorph. material	Zeolite Y, pectolite
52	48	100[3]	30	0.61	0.88	1.89	0.27	0.12	.04 CaO .16 Cl .05 SO_4	21	17	62	*ACD*	Analcite, zeolite X	
53	180	100[3]	30	0.61	0.88	1.89	0.27	0.12	.04 CaO .16 Cl .05 SO_4	21	17	62	*ACD*	Zeolite X	
54	36	180	30	0.61	0.88	1.89	0.27	0.12	.04 CaO .16 Cl .05 SO_4	21	17	62	*ACD*	Zeolite X, microlites	
55	36[2]	360	30	0.61	0.88	1.89	0.27	0.12	.04 CaO .16 Cl .05 SO_4	21	17	62	*ACD*	Leucite, nepheline, orthoclase, pectolite, calcite	Pectolite, microlites ?
51	72	430	30	0.61	0.88	1.89	0.27	0.12	.04 CaO .16 Cl .05 SO_4	21	17	62	*ACD*	Leucite, nepheline, orthoclase	

[1] Letters indicate: *A*—$Al(OH)_3$; *B*—K_3AlO_3; *C*—potassium water glass; *D*—solution containing Na, Ca, Cl, CO_2, and SO_4; *E*—KOH; *F*—K_2CO_3; *G*—CO_2; *H*—labradorite; *I*—Na_2CO_3; *J*—NaCl; *K*—NaOH.

[2] Then filtered 12 hours at the same temperature.

[3] In a glass vessel fitted with a reflux condenser.

[4] Na_2CO_3 added after 24 hrs. heating.

[5] After filtering held for 72 hrs. at 260°C.

potash, because the properties did not correspond exactly to those of pure sodium analcite.

Zeolite A occurred in broad needles with parallel extinction and irregular birefringence which reached a maximum of about .012. Heated in Canada balsam the crystals lost most of their birefringence and at red heat they became cloudy and isotropic. The crystals are probably orthorhombic. The specific gravity, 2.3, and the analysis do not correspond to any known natural zeolite.

Zeolite Y formed in mixtures in the system Na_2O-K_2O-Al_2O_3-SiO_2. The crystals occurred as long needles with a birefringence that was barely visible as the crystals lay on their flat sides, but somewhat higher when they were on edge. The crystals were, therefore, biaxial. $n = 1.478$; specific gravity = 2.3. Easily soluble in HCl.

Zeolite Z in well-formed, clear, thick needles that might be monoclinic, orthorhombic, or hexagonal, but which appeared to be biaxial. Weakly birefringent; $n = 1.495$–1.497. Specific gravity = 2.35. Easily soluble in HCl. The crystals became turbid on heating, but showed a higher birefringence than before. Analysis showed more alkali than any natural zeolite contains, 40%.

Zeolite X formed at 100° to 180° in the system Na_2O-K_2O-Al_2O_3-SiO_2 as monoclinic or orthorhombic needles very similar to zeolite Y. Weakly birefringent; $n = 1.48$ parallel to the c-axis; highest index, 1.485. Specific gravity = 2.17. Easily soluble in HCl.

2. **Leucite,** in orthorhombic (?) prisms with pyramidal terminations and showing very weakly birefringent twinning bands. $n = 1.508$. Many of the crystals contained inclusions of higher index material. Strongly attacked by concentrated HCl, leaving isotropic nuclei.

3. **Nepheline** in very thin hexagonal plates with indices 1.528–1.533.

4. **Potassium feldspar** (**orthoclase**) in crystals showing 3 pinacoids, of which (010) is best developed. $a \wedge c = 67°$. Extinction inclined 3° to the a-axis. Specific gravity = 2.55. $\gamma = 1.525$; $\beta = 1.523$; $\alpha = 1.519$.

5. A **pectolite-like** mineral occurred in sheaves of fine needles as well as in single needles. Its index and birefringence were higher than those of any zeolite. Lost its water readily and shrunk together at dull red heat.

6. A **pyrophyllite-like** mineral was obtained once in very small flakes.

7. A **micaceous zeolite** formed in experiments where there was an excess of CO_2. Platy crystals with a good cleavage. Lost

H_2O, CO_2, and birefringence easily. Weakly birefringent skeletal plates remained after treatment with concentrated HCl. Apparently orthorhombic, biaxial, with small axial angle. An analysis corresponds fairly well to a member of the **gyrolite-centrallasite** group.

8, 9, 10, and 11, **quartz, calcite, microlites,** and amorphous material are not described.

Concluded that **zeolite** formation begins at about 100° C. in the absence of CO_2 and that the upper limit (except for **analcite**) is about 310° under the conditions of the experiments and that equilibrium is rarely reached below 400° in hydrothermal experiments.

They speculate at some length on the regions of stability of the various minerals and conclude that **potassium feldspar** is not formed below 340°, but is formed above 360°, and suggest 360° ± 20° as a point on the geologic thermometer. They suggest the lower limit of albite as another fixed point and would place it at 440°, because at 430° they obtained no albite, while Baur obtained it, apparently from similar solutions at 450°.

They remark that the alkali-aluminum silicates formed in the presence of much free CO_2 seem to correspond more nearly to those formed in nature than do the ones formed in the absence of CO_2.

1920 DITTLER, E.: Über einige experimentelle Versuche zur Bildung
92 silikatischer Nickelerze, *Festschrift C. Doelter, Dresden & Leipzig*, **1920**, 15–27.

Dittler experimented with a nickel-containing *serpentine* and with artificial *olivine* to attempt to determine the conditions of formation of garnierite and the "gray ore" of Frankenstein, a serpentine-like rock in which nickel is concentrated up to about 6.5%. He sought to answer two questions:

(1) Can the nickel be leached from the primary rock and, if so, does garnierite, or the gray ore, form thereby?

(2) Does the nickel ore form directly by weathering, or is there an intermediate product that is rich in magnesium, and poor in nickel?

Experiments were conducted with pure water and with water and CO_2, both with and without pressure:

1. *Experiments without pressure.* Samples weighing 3 g. each of the gray ore with .29% NiO were treated several hours daily with water that contained CO_2, and more CO_2 was supplied constantly from a tank. The temperature was 60° C. At the end of 120 days the residue was 2.4% poorer in MgO than the original material and apparently .65% and .1% richer in SiO_2 and NiO, respectively. These values are not very definite. There were traces of MgO and SiO_2 in the filtrate, but no nickel. On slow

evaporation bunches of **basic magnesium carbonate** crystallized, but no magnesite. The silica was partially separated from the original material as an insoluble gel.

An artificial *olivine* containing 3.49% NiO was treated in the same manner and lost 8% MgO, but gained 2% silica and .24% NiO. Dittler says that under certain conditions such leaching could lead to the formation of silicate nickel ore, since the enrichment in nickel is at least in part due to the taking up of nickel in the silica gel formed by the decomposition of the mineral.

II. *Experiments with pressure.* One gram samples of nickel-bearing serpentine were powdered finer than one millimeter and heated with 100–150 cc. portions of water, of 5% Na_2CO_3, and of 5% H_2SO_4 in sealed glass tubes for several months at 170–178° C. No nickel could be detected in the water after 120 days, and only traces were obtained in the carbonate and acid solutions.

Powdered *garnierite* treated in an autoclave with water at 215–220° C. and 21–23 atmospheres pressure showed an increase from 12.59% to 16.49% NiO, enrichment in H_2O and Fe_2O_3, but leaching of SiO_2, MgO, CaO, and Al_2O_3. The nickel-bearing artificial olivine when treated in the same manner gave a product with 15.11% NiO, after treatment with 10% Na_2CO_3 solution, which dissolved the silica gel. There were fine monoclinic needles in the residue that Dittler thought were probably a **basic magnesium silicate.** He says that the concentration of the NiO seems to be independent of the action of CO_2.

Conclusions:

1. No garnierite was formed experimentally from either nickel-bearing serpentine or olivine, but an amorphous or cryptocrystalline substance more like the gray ore of Frankenstein. The material was enriched in NiO and impoverished in MgO. The experiments show that such processes can form ore in nature, if given enough time.

2. Experiments at elevated temperatures under pressure show that garnierite must be formed by the action of CO_2-bearing groundwater on the bordering rock, and not by the action of rising hot water. (Negative evidence?) The formation of the gray ore, or a similar red ore, is a different but concurrent process, because garnierite cannot form from the gray ore. (More negative evidence?)

3. Extraction of nickel and extraction of magnesium are separate processes and magnesium is apparently extracted first or, at least, more readily.

4. The formation of the nickel silicate ores is a complex problem that needs more study.

1921 **93** KÖNIGSBERGER, J., AND MÜLLER, W. J.: Beschreibung einiger synthetischer Silikatmineralien und synthetischer Versuche nebst Folgerungen für die natürlichen Vorkommen, *Neues Jahrb. Min. Geol.*, Beil. Bd. **44**, 402–59.

A repetition of the experimental results, descriptions of minerals, and comparisons with other work, found in their 1918 paper (91), with a more elaborate discussion of the regions of stability of the minerals and a comparison of natural occurrences in druses and pegmatites with the results of experiments. The extent of the comparison seems to be greater than is justified by the experimental data at hand, although they include the results of other workers in the discussion.

Biotite is said to alter to **chlorite** at about 400° C. and 330° is mentioned as probably about the lowest temperature at which **nepheline** and **kaliophilite** form.

1922 **94** DITTLER, E.: Über einige experimentelle Versuche zur Bildung silikatischer Nickelerze, *Zeit. prakt. Geol.*, **30**, 111–14.

Continuing his earlier experiments Dittler used a nickel-bearing weathered rock from a serpentinized intrusion. He extracted 2 grams of the material, which contained *actinolite*, *anorthite-rich feldspar*, and a little *epidote* and *calcite*, with 200 cc. of water at 90° C., and under a constant pressure of CO_2, for 100 hours. The original material contained 2.76% NiO. The residue after treatment showed small prisms of **nesquehonite** with negative elongation; $\alpha = 1.49$; soluble in dilute HCl. There were also rhombs of **calcite** and silica gel that contained some nickel, but no crystalline magnesite. The residue contained 3.10% NiO. Dissolved silica and magnesia were in about the ratio 1 : 1.

He placed 2 grams of the finely powdered rock in a bomb with 200 cc. of water saturated with CO_2 and heated the mixture for 30 hours at 260° and 40 atmospheres. The residue contained crystalline **magnesite** and **calcite;** also microlites that were taken to be a **nickel silicate.** They were readily dissolved in HCl and the resulting solution gave a nickel reaction. The residue contained 3.95% NiO. The dissolved silica exceeded the dissolved magnesia this time by 4 to 1. This experiment explains why, in the weathering of a nickel-bearing periodotite, magnesium travels farther than the nickel, which is soon fixed as a nickel silicate.

An artificial *olivine* containing 0.5% NiO was treated in the same manner at 265° and 40 atmospheres. Fresh solvent was added each 30 hours until there was no further change in the nickel content. The final NiO content of the residue was .97%. Dittler thinks that nickel ore can be formed by leaching of SiO_2 and MgO at atmospheric pressure, if enough time is available. Theoretical

equations show that a talc-like product should also be formed. Parageneses of the minerals in natural deposits seem to confirm this hypothesis, he says.

1922 **95** MOREY, GEORGE W.: Solubility and decomposition in complex systems, *J. Soc. Glass Tech.*, **6**, 20–9.

It is shown, by using the system H_2O-K_2O-Cr_2O_3 with the 30° isotherm represented, that a compound has no true solubility in water at a given temperature unless the tie line joining the point that represents the composition of the compound to the point representing water cuts the saturation curve of the compound. In all other cases the compound is decomposed by water.

This principle is then applied to silicate systems, using as an example the system H_2O-K_2SiO_3-SiO_2 with the isotherms from 200° to 600° represented. This system illustrates why it is that, although silicates may have a true solubility in water at high temperatures, they are decomposed by water at ordinary temperatures. Therefore, it is erroneous to speak of the solubility of silicate mixtures in water whether they are crystalline, or in part or wholly glassy, unless it has been shown experimentally that such compounds or mixtures do have a true solubility in water at the temperature under consideration, and are not merely decomposed by it.

1923 **96** SCHWARZ, R., AND BRENNER, A.: Über synthetische Aluminiumsilicate und deren Beziehungen zum Kaolin, *Berichte deut. chem. Gesell.*, **56**, 1433–37.

Schwarz and Brenner precipitated a silica-alumina gel by mixing neutral solutions of $AlCl_3$ and Na_2SiO_3. They performed four series of experiments to determine the effect on the composition of the precipitate of (1) concentration, (2) ratio of alumina to silica in the solutions, (3) time, and (4) temperature. The first three series were performed at 20° C.

(1) *Effect of concentration.* They found the silica content of the precipitate to increase with increasing concentration of the solutions used, Al_2O_3 : SiO_2 being 1 : 2.64 for the highest concentrations used (ca. 1.8% solutions) and 1 : 1.57 for the lowest concentrations used (ca. .17% solutions).

(2) Even with the dilute solutions the silica content of the precipitate increased as the amount of silica in the original mixture was increased, until the ratio Al_2O_3.: SiO_2 reached 1 : 6, after which the composition of the precipitate was approximately constant at $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. This composition led them to expect kaolinite to be formed from the gel. The ratio 1 : 6 in the original solution is thought to be significant, because that is the

1924 **97**

Al_2O_3 : SiO_2 ratio in the " acidic " feldspars from which kaolin is commonly derived.

(3) The silica content of the precipitate increased with increasing time of flocculation until it became approximately constant after 192 hours, no further change being observed in 500 hours. This precipitate, dried at 110°, had the composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

(4) Some of the solutions were boiled for 1 to 3 hours and the resulting precipitates allowed to stand for 2 to 21 days, after which the products were more or less crystalline and gave X-ray patterns similar to that of kaolinite. Neither diagrams nor tables of lines are given, however. For the charges that were partly crystalline they suggest two possibilities: (1) the heat partly crystallized the alumina, or (2) there was insufficient time for all of the precipitate to change to kaolinite. (Later work makes it seem probable that all of the crystalline material was a hydrate of alumina, possibly **boehmite.**)

Dehydration of the artificial material did not agree closely with that of natural kaolinite. The natural mineral loses its water continuously between 360 and 640° C. The artificial material lost one molecule of water below 260°, practically none between 260° and 360°, and lost the other molecule between 360° and 640°. This difference may be due to the fact that their product had not had time to incorporate the second molecule of water in its structure. Neither dehydration curves nor tables of data are given.

They conclude that mixtures in the system Al_2O_3-SiO_2-H_2O with Al_2O_3 : SiO_2 = 1 : 6, or richer in silica, in dilute, neutral solution yield only one " compound," $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

1924 **97** SCHOTT, G., AND LINCK, G.: Über die Hydration natürlicher und künstlicher Gläser, *Koll. Zeit.*, **34**, 113–16.

Schott and Linck treated samples of eight different *glasses* in an autoclave with 400 cc. of water at 243° C. and 35 atmospheres pressure. 200 gram samples passed through a 200 mesh sieve onto a 250 mesh sieve were used. They were heated about 30 days, stirred well from time to time, and a 3 g. sample taken out for analysis after each stirring. The samples were dried in open air, then analyzed for water by heating to 1000° and taking the water off into a calcium chloride tube.

The values thus obtained obviously do not represent hydration, or solution, because rates and amounts of decomposition of the glasses were not determined, and much of the water must have remained adsorbed on the very fine particles under atmospheric conditions.

Artificial *glasses* ranging in composition from granitic to peridotitic took up from 6% to 18% water, the more basic glasses taking up more water. Dehydration of the treated artificial peridotitic glass showed a loss of 10.75% water below 100° C.; therefore, the amount really in solution in the glass could not have been more than 7.25%, instead of the 18% shown in the graph on p. 115 of the original paper. Hydration of an artificial basaltic glass proceeded more rapidly when the sample was stirred frequently.

A natural *pitchstone* lost 6% water fairly regularly below 450°. A natural *obsidian* lost .2% water below 800° and .1% more between 800° and 1040°.

1925 **98** EITEL, W.: Die experimentellen Hilfsmittel zur Mineralsynthese unter hohen Drucken und hohen Temperaturen, *Fort. Min. Krist. Petr.*, **10**, 157–86.

A review of the apparatus used for the synthesis and study of minerals under conditions of high pressures and temperatures. It begins with the apparatus of Sir James Hall and includes most of the important developments since that time. Numerous pictures and diagrams are given.

1925 **99** SCHWARZ, R., AND WALCKER, R.: Über die Genesis der natürlichen Aluminiumhydrosilicate, *Zeit. anorg. Chem.*, **145**, 304–10.

Schwarz and Brenner (96) had prepared a silica-alumina gel by co-precipitation from solutions in which the ratio of alumina to silica was 1 to 6. The precipitate had the composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ after drying, and it eventually crystallized to a kaolin-like substance.

Schwarz and Walcker experimented further with solutions of $AlCl_3$ and Na_2SiO_3, keeping the ratio $Al_2O_3 : 6SiO_2$ because that is the ratio in potassium feldspar. They varied the pH value from 4.10 to 9.25 and concluded that for **kaolinite** formation the pH value must lie between 4.5 and 5.2 and that the best range is 4.8 to 5.0. They tried other aluminum salts and concluded that the nature of the anion is without effect on the results. H_2SiO_3 (from Na_2SiO_3) gave values slightly below 2 for silica (2 molecules of silica to 1 of alumina), while $H_4Si_3O_8$ (from $Na_2Si_3O_8$) gave values slightly over 2. They believe that $H_2Si_2O_5$ would give values nearer 2 than either of the other compounds gave.

Time had some effect on the results, the ratio becoming $Al_2O_3 : 3SiO_2$ after 2 months. This formation of a silica-richer substance is thought to be analogous to the formation of **allophane** in nature. It may be due to adsorption of silicic acid by the first formed precipitate.

Schwarz and his co-workers incline toward the belief that there is a preliminary hydrolysis of feldspar, and then a recombination

of some of the products ("**prokaolin**") to form kaolin, rather than a direct alteration of feldspar to kaolin.

1925 **100** WEIL, R.: Synthèse de la cristobalite par voie humide, *Compt. rend.*, **181**, 423–4.

Experiments were performed in a steel tube with 4 g. of anhydrous precipitated silica to which dilute Na_2SiO_3 was added to serve as a mineralizer. The temperature ranged up to 750° C. **Cristobalite** did not form below 650°, nor from solutions in which the concentration was equivalent to more than 1 part of NaOH per 100. From more concentrated solutions only **quartz** formed. The **quartz** crystals were fusiform and about 1 mm. long. Smaller filiform crystals were observed in some charges and may have formed at lower temperatures, perhaps during cooling.

Cristobalite that formed from runs when nearly all of the liquid escaped was in crystals that showed cubes and octahedra and were .05–0.1 mm. in diameter. Where there was only partial escape the crystals were smaller and rounded, possibly due to partial resolution during cooling(?). $n = 1.487$. Specific gravity = 2.32. The transformation of cristobalite to the isotropic form, which lags about 20° on cooling, as does that of natural cristobalite, takes place at temperatures from 200–260°. Weil believes that there is some dependence of this temperature on the concentration of the charge from which the cristobalite formed.

In some of the charges, from which all of the water had escaped, there were crystals, either isolated or in masses, that looked like **tridymite,** but had the index and inversion point of **cristobalite.** They may be pseudomorphs of **cristobalite** after tridymite, or platy crystals of **cristobalite** that look like tridymite. No tridymite was positively identified in any of the runs.

1927 **101** IPATIEFF, W., AND MOUROMTSEFF, B.: Formation de silicates cristallisés en millieu aqueux sous pressions et à températures élevées, *Compt. rend.*, **185**, 647–9.

Silicic acid gel was emulsified with water, placed in a silver tube in a bomb charged with H_2 or CO_2, and heated for 2 or 3 days at constant temperature. Silica gel thus treated for 30–40 hours at 310–320° under a pressure of 200 atmospheres of H_2 gave **quartz** with typical prisms and "pyramids."

When CO_2 was used instead of H_2 a "**well-crystallized hydrate, $5SiO_2 \cdot 3H_2O$**" was obtained. (No properties of these "crystals" are given, but it seems highly probable that the crystalline product was one of the anhydrous forms of silica and that incomplete separation from the hydrous gel led to the formula showing water.)

Several crystalline silicates were prepared in similar experiments. A co-precipitated silica-magnesia gel, precipitated in the

presence of an excess of the magnesium salt, and heated for 2 days at 300° under a pressure of 250 atmospheres of H_2, gave a product like **amianthus.** It was fibrous, with an unctuous feel, and slightly birefringent. Analyses showed 58–67% SiO_2, 24–15% MgO, and 7–10% H_2O. A silica-lime gel under the same conditions produced birefringent needles of a **calcium silicate.** Analysis showed 85.2% SiO_2, 7.2% CaO (+ Na_2O), and 7.8% H_2O.

A similar gel with manganese heated for 2 days at 300° C. and under a pressure of 180 atmospheres of hydrogen produced well-formed transparent prisms (**manganese silicate**?) with very high birefringence. Composition was variable. When all of the soluble manganese salt was washed out of the gel it " hydrolyzed " to form the supposed crystalline hydrate of silica, $5SiO_2 \cdot 3H_2O$.

A gel containing zinc, well washed before treatment (presumably under the same conditions as the gel containing manganese), gave large, clear prisms (**zinc silicate**?) with pyramidal terminations. They contain 7.3% ZnO.

The authors state that they have also prepared in this manner **silicates of aluminum and iron,** concerning which they will report later.

1927 **102** KÖNIGSBERGER, J.: Experimentelle Hilfsmittel der hydrothermalen Synthese bei hohen Temperaturen und Drucken, *Fort. Min. Krist. Petr.*, **11**, 41–8.

A description of several types of apparatus in which water vapor develops the pressure, which were neglected by Eitel (98). Pictures and diagrams are given.

1927 **103** LEONARD, R. J.: The hydrothermal alteration of certain silicate minerals, *Econ. Geol.*, **22**, 18–43.

Leonard performed experiments to determine the effect of various solutions at various temperatures on several *feldspars* and on *spodumene*, attempting especially to produce sericite, kaolin, and alunite. The minerals used were ground to pass a 200 mesh sieve. The experiments were performed either in Pyrex flasks or sealed Pyrex tubes. Blank tests indicated that the glass probably did not affect the results. Identification of the products was largely by means of X-rays, supplemented by measurements of indices of refraction and approximate birefringences. Diagrams from microcline, alunite, bytownite, and cryolite are included for comparison with the five diagrams given from experimental products, but no tables of the lines are given.

The experiments are listed in the following groups:

I. 0.05 M solutions of K_2CO_3, Na_2CO_3, KCl, NaCl, K_2SO_4, and Na_2SO_4 at 100° C. for 14 days had no effect on *microcline, labra-*

dorite, or *spodumene*. The sulfates corroded *albite* and *bytownite* slightly, but these two minerals were not affected by the other solutions. 0.05 M HCl partly (10%) decomposed *labradorite*, but did not attack any of the other minerals. 0.05 M H_2SO_4 decomposed 90% of the *labradorite* and 80% of the *bytownite*, leaving in each case amorphous silica as the solid product. In each experiment in this group one liter of solution and one gram of material were used and every 24 hours 250 cc. of the solution were siphoned off and that much fresh solution added.

II, III, and IV. One gram samples of *microcline*, *albite*, and *bytownite* were treated with 500 cc. portions of 0.05 M solutions of H_2SO_4, K_2SO_4, and Na_2SO_4, to each of which had been added 50 g. of aluminum sulfate; other such samples were treated with 500 cc. portions of 0.05 M $Al_2(SO_4)_3$ solution. At 100° for 7 days the minerals were 50–99% altered to **alunite;** at 65° for 60 days the results were much the same; at 22° for 60 days the minerals were 40–60% changed to **alunite.** No distinction is made between potassium alunite, natroalunite, or isomorphous mixtures of the two. Blank tests with aluminum sulfate and either alkali sulfate also yielded alunite, but smaller amounts than when one of the feldspars was also present.

V. One gram charges of *microcline*, *albite*, and *bytownite* were heated in sealed Pyrex tubes of 60 cc. volume with 15 cc. portions of 0.1 M solutions of H_2SO_4, K_2SO_4, and Na_2SO_4, to each of which 3 g. of aluminum sulfate had been added; also half gram samples of the minerals with 15 cc. portions of molar aluminum sulfate solution. The mixtures were heated for 7 days at 200° C., at which temperature the pressure was approximately 15 atmospheres. The minerals were 60–90% altered to **alunite.**

VI. Conditions as in V, except that 0.2 g. samples of the minerals were used with molar solutions. The results of this group of experiments are recorded in the following table:

Solution	Microcline	Albite	Labradorite	Bytownite
K_2CO_3		Phillipsite?	Phillipsite?	Phillipsite
$KHCO_3$		No change		
Na_2CO_3	Thomsonite?			Mordenite?
$NaHCO_3$	Slight corrosion	Much corrosion		
KCl			No change	
NaCl	No change			
HCl	Dissolved			
H_2SO_4	60% silica	40% dissolved; rest corroded	99% silica	60% dissolved
K_2SO_4		No change		
Na_2SO_4	No change			

VII. 0.2 g. of microcline, 0.2 g. of AlF_3, and 0.2 g. of Na_2SiF_6, all as solids, when heated in a sealed Pyrex tube of 50 cc. volume with 0.1 g. of water for 20 hours at 400° (about 8 atmospheres pressure) yielded 90% **cryolite.**

VIII. Conditions the same as in VII, except that the temperature was 575°, which produced a pressure of about 10 atmospheres. *Microcline*, with KF and Na_2SiF_6, gave 25% **leverrierite** (?). *Microcline*, with AlF_3 and Na_2SiF_6, gave 40% **cryolite.** *Labradorite* with K_2CO_3 gave 40% **leverrierite** (?). *Bytownite* with K_2CO_3 gave 40% **leverrierite** (?).

IX. Half gram samples with one gram portions of each of the reagents indicated, at 350° in superheated steam at one atmosphere for 9 hours, gave the following results:

Microcline, *albite*, or *bytownite*, with KF and Na_2SiF_6, gave 40–50% **phillipsite** (?). The same minerals with $AlCl_3$ and Na_2SiF_6 yielded 20–40% **cryolite.** A blank test with AlF_3 and Na_2SiF_6 failed to produce cryolite under the conditions of the experiments.

Microcline, or *albite*, with $AlCl_3$ gave 60% **leverrierite** (?). *Albite*, or *bytownite*, with KCl and $AlCl_3$, gave 50–70% **leverrierite** (?). *Microcline*, or *albite*, with NaCl and $AlCl_3$, gave 60–50% **leverrierite** (?).

X. Like IX, except the samples were held at 500° for 9 hours. *Microcline* with KF and AlF_3 gave 80% **phillipsite** (?); with KF and Na_2SiF_6 it yielded 60% silica; with AlF_3 and Na_2SiF_6, 90% **cryolite.**

Conclusions:

(1) Hot acidic solutions in nature attack and decompose minerals and rocks. The experiments indicate that silica is probably left behind, but that most of the alumina is carried away with the more soluble constituents.

(2) Soluble aluminum sulfate is probably required for the formation of **alunite,** since solutions of aluminum sulfate alone produced it from feldspar, but sulfuric acid and the alkali sulfates did not.

(3) The experiments suggest that **cryolite,** which has commonly been considered to be of pegmatitic origin, may be formed by the hydrothermal alteration of feldspar.

(4) Fluorides may be active in **sericitization.**

(5) **Leverrierite** forms more readily in the presence of chlorides than of fluorides.

(6) No kaolin could be detected in any of the experiments. It may have been present in small amounts, but was not one of the

principal products. Leonard believes that its formation in nature is due largely to the weathering of aluminous minerals under atmospheric conditions, but says that it is quite possible that unknown factors may enable kaolin to be formed by the action of hydrothermal solutions.

1927 **104** MOREY, GEORGE W., AND BOWEN, N. L.: The decomposition of glass by water at high temperatures and pressures, *J. Soc. Glass Tech.*, **11**, 97–106.

Samples of various *glasses* were heated with water in steel bombs for about 20 hours, cooled and the products examined. Two series of experiments were performed: (1) At 300° C. 18 cc. of water were used in bombs with a free volume of 40 cc., insuring the presence of liquid during the runs. (2) At 550° 10 cc. of water were used in each experiment. With the exception of the samples of tubing (Nos. 19–24) the glasses were introduced as cubes approximately one centimeter on a side.

In these experiments the original materials were homogeneous and their compositions were known. The compositions are, in general, not near those of natural magmas, but the results represent a considerable range of composition from which the forms of silica crystallize under hydrothermal conditions. The compositions of the glasses are given in Table II. Several unknown crystalline phases appeared in the various glasses. They are described briefly in Table I, below, principally for reference and comparison by other workers. All the glasses were more attacked at the higher temperature.

These results are excellent examples of Morey's thesis (95) that the action of water on glass is primarily one of decomposition.

TABLE I. SUMMARY OF THE EXPERIMENTAL WORK.

No.	300°	550°
	Crowns	
1	Quartz and amorphous material	Quartz and an unknown crystalline phase; fibrous to needle crystals; inclined extinction; indices 1.54–1.55
2	(1) Quartz (2) needles with negative elongation; $\alpha = 1.46$, $\gamma = 1.54$, biaxial, $2V$ nearly 90°	(1) Quartz (2) crystals like No. 1 at 550°
3	Quartz and much amorphous material	Quartz and indefinite material
	Borosilicate Crown	
4	Crystals with low birefringence; $n = 1.550$ Outlines rhombic or hexagonal	Quartz and needles with inclined extinction Indices 1.54–1.55

(*Table continued on next page*)

TABLE I (*Continued*).

No.	300°	350°
	Barium Crowns	
5	Definite but indeterminate crystallization	Crystals of $BaO \cdot 2SiO_2$
6	$BaO \cdot 2SiO_2$ negative elongation, $\alpha = 1.60$; $\gamma = 1.62$	
7	Crystalline $BaO \cdot 2SiO_2$	Definite but indeterminate crystallization
8	Spherulites—mean index 1.60–1.62 Probably $BaO \cdot 2SiO_2$-$2BaO \cdot 3SiO_2$ solid solution	Definite but indeterminate crystallization
9	Crystals with hexagonal outline; uniaxial, negative; $\epsilon = 1.54$; $\omega = 1.68$	(1) $BaO \cdot 2SiO_2$ (2) undetermined crystals
10	Spherulitic crystals; $n_m = 1.64$	Definite but indeterminate crystallization
	Flints	
11	(1) Quartz (2) needles with slightly inclined extinction, positive elongation, $\gamma = 1.70$, $\gamma - \alpha = .015 - .020$	(1) Tridymite or cristobalite, or both, but no quartz (2) crystals like (2) at 300°
12	(1) Quartz (2) uniaxial negative crystals with $\epsilon = 1.730$, $\omega = 1.75$–1.76 (3) crystals like (2) of No. 11	(1) Quartz (2) like (2) of No. 11
13	(1) Quartz (2) crystals with parallel extinction, $\gamma = 1.730$, $\gamma - \alpha = .015$ (3) like (2) of No. 11	Large quartz crystals. Charge melted to a glass with the index higher than the original (1.563) and containing 2.6% water
14	Uniaxial negative crystals	
15	(1) Quartz (2) plates, hexagonal in outline, uniaxial negative, $\omega = 1.735$; $\epsilon = 1.725$	Crystals like (2) at 300°
16	Uniaxial negative crystals with $\epsilon = 1.730$, $\omega = 1.76$	Crystals like those at 300°, but seem to have somewhat lower indices
17	(1) Alamosite, $PbO \cdot 2SiO_2$ (2) hexagonal plates, uniaxial negative, $n = 1.74 - 1.76$	(1) Alamosite (2) hexagonal plates like those at 300°
18		Alamosite
	Tubing	
19	Small monoclinic crystals with $n = 1.530$ (2) rare large crystals, uniaxial negative, $\epsilon = 1.50$; $\omega = 1.62$	Needles of $Na_2O \cdot 3CaO \cdot 6SiO_2$ (devitrite)
20	(1) Quartz (2) amorphous material	
21	(1) Quartz (2) poor shreddy crystals $\alpha = 1.46$; $\gamma = 1.54$, biaxial, $2V$ is nearly 90°	Needles of $Na_2O \cdot 3CaO \cdot 6SiO_2$ (devitrite)
22	Indeterminate spherulites	(1) Much tridymite (2) needles with parallel extinction; positive elongation; probably $Na_2O \cdot 3CaO \cdot 6SiO_2$
23	Indeterminate crystallization	Few needles like (2), No. 22, at 550°
24	(1) Large rounded grains with spherulitic structure and $n = 1.472$. Weak birefringence. (2) H_3BO_3 deposited from the solution on cooling	(1) Tridymite (2) H_3BO_3

TABLE II. COMPOSITIONS OF THE GLASSES

No.	n_D	SiO_2	B_2O_3	K_2O	Na_2O	CaO	BaO	ZnO	PbO	Al_2O_3	As_2O_3
					Crowns						
1	1.5136	71.2	0.5	14.4	5.5	6.5	—	1.2	—	—	0.7
2	1.5194	71.0	—	9.0	8.0	8.0	2.6	—	—	—	1.4
3	1.5220	71.5	—	5.6	7.1	10.4	—	4.3	—	—	1.1
4	1.5117	70.8	7.2	14.4	5.4	2.0	—	—	—	—	0.2
					Barium Crowns						
5	1.5651	48.9	3.7	4.3	4.4	—	28.5	8.9	—	1.0	0.3
6	1.6109	35.0	9.0	—	—	—	40.8	8.4	—	6.4	0.1
7	1.6115	35.0	8.9	—	—	—	40.8	8.4	—	6.4	0.5
8	1.6128	35.5	9.1	—	—	—	42.2	8.5	—	4.3	0.4
9	1.6133	30.8	9.3	—	—	—	42.5	8.7	1.6	6.6	0.5
10	1.6173	35.6	9.1	—	—	—	42.0	8.5	—	4.3	0.5
					Flints						
11	1.5328	65.8	—	1.4	14.8	2.6	—	1.6	13.2	—	0.6
12	1.5413	64.5	—	2.1	9.8	1.4	—	—	21.9	—	0.3
13	1.5516	60.2	—	6.0	7.0	—	—	—	26.4	—	0.4
14	1.6055	47.9	—	4.8	4.4	—	—	—	42.4	—	0.5
15	1.6243	45.8	—	4.6	4.0	—	—	—	45.0	—	0.6
16	1.6486	41.3	—	6.0	—	—	—	—	52.4	—	0.3
17	1.7233	32.8	—	4.1	—	—	—	—	62.6	—	0.5
18	1.7572	29.4	—	2.4	—	—	—	—	67.1	—	1.0
					Tubing						
19	Imported soft tubing; A. H. Thomas, origin unknown										
20	Soft domestic tubing; origin unknown										
21	Kimble lime tubing										
22	Kimble "Perfection"										
23	Jena combustion										
24	Pyrex										

1929 **105** EITEL, W., AND SKALIKS, W.: Hochdrucksynthesen von Carbonaten und Silicaten, *Naturwiss.*, **17**, 316–19.

Another review of various types of apparatus.

1929 **106** GRUNER, E.: Untersuchungen an Alkali-Aluminium-Silicaten. I. Synthetische Studien am Nephelin, *Zeit. anorg. Chem.*, **182**, 319–31.

Half gram samples of *muscovite* and *paragonite* were treated in a bomb with 20 cc. portions of N/2 KOH and NaOH, whose contents of alkali were accurately known, at different temperatures and for different lengths of time. **Nepheline** and mica were identified in the products, but no properties are given. It was not possible to separate the minerals because of the smallness of the grains and the slight difference in specific gravity. However, nepheline is soluble in HCl and mica is not, so the Al_2O_3 of the nepheline was determined by dissolving it out in HCl. The equivalent amount

of alkali was calculated and the amount of alkali used up during the run was determined. If these two values agreed fairly closely they gave a fair approximation of the amount of **nepheline** formed.

In 100 hours at 200° C. *muscovite* with an excess of KOH gave 24% **kaliophilite;** at 300°, 72%; at 400°, 88%. Preliminary ignition affected the initial rate of reaction considerably, but the ultimate yield very little. There was no formation of kaliophilite at 100°.

Identifications were by chemical and optical methods. Two photomicrographs of the artificial nepheline are given.

In 100 hours at 200° with an excess of NaOH *paragonite* gave 60% **nepheline;** at 300°, 92%; at 400°, 98%. Ignition had the same effect as on muscovite. The more ready transformation of paragonite is in harmony with the facts that muscovite is the most stable mica and that muscovite itself takes up Na_2O more readily than it does K_2O. The work of Königsberger and Müller (93), who obtained no nepheline below 330°, is cited; the apparent discrepancy is supposed to be due to different materials being used.

In all of the experiments, especially at 400°, **natrolite** and other **zeolites** appeared. They were identified microscopically, but no attempt was made to separate them chemically from the other products. They therefore introduced a small error in the determinations of the amounts of **nepheline** formed. They were probably formed, the authors think, not directly from the mica, but by secondary reactions.

No reversal of the reactions was observed at 200° or 300°, but at 400° there were small plates of **muscovite** that might have been formed from the *kaliophilite* by reversal. The quantity of **muscovite** was not determined. No such reversal was observed with nepheline alone. Gruner and Hirsch agree with Königsberger and Müller that the lower temperature boundary for the formation of **mica** is about 400°.

Zeolites formed from both *nepheline* and *kaliophilite*. **Nepheline** was also prepared by fusion of *kaolin* and solid alkalis.

1929 107 VAN NIEUWENBURG, C. J., AND PIETERS, H. A.: Studies on hydrated aluminum silicates. I. The rehydration of metakaolin and the synthesis of kaolin, *Rec. trav. chim.*, **48**, 27–36.

Natural *kaolin* treated with saturated steam at 50 to 125 atmospheres lost a part of its water. No explanation is offered.

Rehydration of *metakaolin* (partially dehydrated kaolin) reached equilibrium in about 48 hours and the extent of the rehydration depended upon the temperature to which the kaolin had been heated, and upon the time that it was held at a given temperature, being less for higher temperature of treatment and for

longer times of heating. For example, *kaolin* heated to 420° C. would then take up 14.5% water, but if it had been heated to 1000° it would take up 11%; to 1050°, 3%; to 1500°, 1%.

Alumina that had been ignited at 1000° took up 16–17% water, giving a compound of the composition $Al_2O_3 \cdot H_2O$ which was only slightly attacked by HCl; specific gravity = 3.06; $n = 1.65$ (**boehmite**?). The compound is weakly birefringent. Neither ignited alumina nor mixtures of it with silica in the ratio of 1 : 2 took up water in the same manner in which the *metakaolin* did, from which the authors concluded that metakaolin is not a mixture of alumina and silica, as postulated by Mellor, but is probably a compound, perhaps $Al_2Si_2O_7$.

Synthesis of Kaolinite.—Van Nieuwenburg and Pieters repeated the work of Schwarz and Brenner, but obtained no kaolinite. Gels prepared according to the directions of Schwarz and his co-workers were richer in silica than $Al_2O_3 \cdot 2SiO_2$. They prepared gels by using 5 liters of a solution containing 130 mg. of SiO_2 per 10 cc. and mixing it with 5 liters of a solution containing 260.4 g. of $AlCl_3 \cdot 6H_2O$. The mixture was neutralized with dilute NaOH, using litmus as an indicator. The precipitate, after drying at 110°, contained about 20% water (6% more than kaolinite contains), and an $Al_2O_3 : SiO_2$ ratio of practically 1 : 1.

Autoclaving in steam at 110 atmospheres for 144 hours reduced the water content to about 10%. At 200–260 atmospheres for 288 hours the water content was reduced to 9%. This reduction below the theoretical amount is not to be taken as evidence that the product is not kaolinite because the preliminary experiments showed that kaolin itself loses water under similar treatment in an autoclave with steam.

The alumina of the original gel was completely soluble in HCl, but treatment at 200–260 atmospheres (367–383°?) in steam reduced the solubility to 4.7%. This is taken to indicate a combination of the alumina with silica. The final product is 95% crystalline and the properties agree closely with those of **kaolinite;** specific gravity = 2.68; $n = 1.56$; weakly birefringent.

Summary: *Metakaolin* prepared below 850° takes up water under a steam pressure of 100 atmospheres practically to the original kaolin composition.

Alumina ignited at 1000° takes up water under like conditions to form a monohydrate, but ignited alumina and silica mixed in the proper proportions do not behave like metakaolin.

The products of Schwarz and his co-workers were not kaolinite, but become **kaolinite** if they are heated under 200–260 atmospheres steam pressure (at 367–383°?) for a long time.

1929 **108** SCHWARZ, R.: Über die Synthese von Kaolin, *Rec. trav. chim.*, **48**, 695–6.

In answer to van Nieuwenburg and Pieters (107) Schwarz says that he did not maintain that he had prepared true kaolinite, but a compound with the same formula, which gave a similar X-ray diagram. He believes that the work of van Nieuwenburg and Pieters supports his theory that *feldspar* yields primary decomposition products that recombine in the proper proportions to form **kaolinite.**

1929 **109** WELLS, F. G.: The hydrothermal alteration of serpentine, *Am. J. Sci.* (5), **18**, 35–52.

Wells prepared " one of the hydrous silicates resembling **serpentine,** although insoluble in acids " by heating 2 cc. of water glass that contained 0.5 g. of SiO_2 per cc. in 10 cc. of water with 1 g. of " magnesia alba " ($MgCO_3$ with a little $Mg(OH)_2$ and H_2O). The positive results were as follows:

Exp. No.	Temp. °C.	Pres. Atm.	Time, Days	Observations
IV	375	200	3	Slight change to a serpentine-like substance
V	475	321	2	Complete change to a serpentine-like substance
VI	310	97	7	A hydrous silicate was produced

Several experiments were performed in the attempt to produce serpentine from *olivine.* Samples of *olivine* were treated with solutions of various salts and acids at temperatures from 100° to 520° and under pressures from 1 to 301 atmospheres for times ranging from 9 hours to 15 days. Varying degrees of solubility (decomposition?) of the olivine were obtained, but no serpentine was produced. Wells concludes that the alteration of olivine to serpentine is a high temperature deuteric effect. Lower temperature serpentinization may take place by reaction of siliceous solutions with magnesium carbonate rocks. (As low as 375° C., and under a pressure of 219 atmospheres, according to the experiments.)

1929 **110** THORVALDSON, T., AND SHELTON, G. R.: Steam curing of Portland cement mortars. A new crystalline substance (Preliminary Paper), *Can. Jour. Research*, **1**, 148–54.

Studied the effect of curing cement in saturated steam at 100°, 125°, 150°, 175°, and 200° C., both as to effect on strength and changes in crystalline phases. Rate of hydration, as shown by the rate of disappearance of the original crystalline phases, was more rapid at the higher temperatures. Hexagonal plates of **$Ca(OH)_2$** appeared almost at once in any given run, increased to a maximum at a time that depended on the temperature of the run, and then

decreased as the amount of a new crystalline phase increased. The $Ca(OH)_2$ disappeared entirely in all runs where enough time was allowed.

The **new crystalline phase** appeared at different temperatures in different cements, appearing in one run at 100° C. Runs at 175° C. produced the largest amounts of this compound, and the materials from these runs showed the greatest increases in strength, and the greatest resistance to the action of sulfate solutions. The crystals of the new phase were thin, elongated plates, commonly with square ends, but sometimes bevelled. $\alpha = 1.614; \beta = 1.620; \gamma = 1.633$ (All values $\pm .002$). Biaxial, positive; $2V = 68°$ (Calculated from indices). Positive elongation. Penetration twins common.

This compound is decomposed readily by dilute HCl; when H_2SO_4 is added much **gypsum** is formed. It is decomposed slowly by a solution of $MgSO_4$, but is not attacked by solutions of NaOH, Na_2SO_4, or $CaSO_4$. Dehydration begins at about 400° C., but is not complete after prolonged heating at 650° C.

(The composition is not given, but the optical properties are very similar to those of **afwillite.**)

1930 VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B.: Über die
111 Flüchtigkeit der Kieselsäure mit Wasserdampf, *Rec. trav. chim.*, **49**, 857–60.

Half gram samples of the various forms of silica were placed in small gold crucibles within copper tubes. One gram samples of ZnO (2 g. in the experiments in which amorphous silica was in the lower crucible) were placed in copper crucibles near the tops of the copper tubes. In a given experiment a copper tube with its crucibles and their charges was placed in an autoclave with enough water in the autoclave and copper tube to develop a pressure of 300 atmospheres at 395° C. After 24 hours under these conditions the quartz in the lower crucible lost 52.6 mg. In other experiments under the same conditions tridymite lost 204 mg.; cristobalite, 118 mg.; and amorphous silica, 295 mg.

Most of the silica that left the lower crucibles was fixed in the ZnO of the upper ones. For example, 46 mg. of the 52.6 mg. lost by the quartz were recovered in the upper crucible, and 280 mg. of the amorphous silica. The amount of transport was found to increase with increasing fineness of the silica particles. The transfer is attributed to " volatile transport " of the silica by super-critical steam (= gaseous solution of silica in super-critical steam?).

1930 GRUNER, J. W.: Hydrothermal oxidation and leaching experi-
112 ments; their bearing on the origin of the Lake Superior hematite-limonite ores, *Econ. Geol.*, **25**, 697–719 and 837–67.

Gruner records numerous hydrothermal leaching and oxidation experiments that are supposed to have a bearing on the manner of formation of the Lake Superior iron deposits.

He made measurements on the solubility of quartz, chalcedony, and silica gel at 200–300° C. See the graph, Fig. 11, for his quantitative results and for a comparison with the results of other workers.

1930 SMITS, A.: Das System Wasser-Siliziumdioxide, I, *Rec. trav. chim.*,
113 **49**, 962–6.

A theoretical paper supplying the physico-chemical background for the work of van Nieuwenburg and Blumendal (111), or rather being Smits' " opinion on the physico-chemical principles underlying this phenomenon."

1931 PERMJAKOFF, W. M. Kaolinsynthese, *Iswestija Nautschnoi Komis-*
114 *sii* (Nachrichten der wissenschaftlichen Kommission für Land- und Volkswirtschaft beim S. N. K. der U. S. S. R.) 1. Ausgabe. Leningrad 1931, S. 69. (Abstract from a discussion by Noll, *Min. Pet. Mitt.*, **45**, 1934, p. 189.)

Noll says that these experiments were performed at higher temperatures and pressures than his and that the chemical and optical properties of the product are well comparable to those of **kaolinite** itself.

The X-ray diagram is not identical with that of natural kaolinite, nor with that of the synthetic kaolinite prepared by Noll. The diflerences may be due to different temperatures of formation.

1931 VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B.: The pneu-
115 matolytic synthesis of silicates, I, *Rec. trav. chim.*, **50**, 129–38.

Using apparatus like that employed in their earlier experiments on the solubility of silica in super-critical steam (111), Van Nieuwenburg and Blumendal continued their work, paying attention particularly to the minerals formed. They used oxides of various metals in the upper crucible and, in duplicate experiments each time, amorphous silica and FeSi (60% Si) in the lower crucible. The results were identical in each set of duplicate experiments, except in the case of PbO and FeSi, when most of the oxide was reduced to metallic **lead,** presumably by the action of hydrogen evolved by the action of steam on the FeSi. No definite minerals were obtained with BaO, FeO, Fe_2O_3, BeO, Al_2O_3, CuO, although each oxide took up a small amount of silica.

The crystalline products, which always formed in the upper crucible, were identified microscopically; photomicrographs of most of them are given. The table below indicates in which experiment each mineral was formed and gives a summary of the properties of each.

TABLE OF RESULTS (115).

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Materials Used	T.(°C.)	P.(atm.)	Time	Mineral(s) Formed	Indices	Crystal Form	Other Properties
200 mg. CaO 1 g. SiO_2 or 5 g. FeSi	365	200	2 da.	Beta wollastonite (+ $CaCO_3$ from impurities)	1.620– 1.630	Needles	Feebly biref. Parallel ext.
200 mg. $Sr(OH)_2$ 1 g. SiO_2 or 5 g. FeSi	365	200	2 da.	$SrSiO_3$ (some $SrCO_3$ from impurities)	1.595– 1.610	Hexagonal plates	
1 g. PbO 1 g. SiO_2	395	300	3 da.	Alamosite	Very high	.01 to .1 mm. prisms	Sol. HNO_3 Distinct biref. S. G. = 6.4
1 g. PbO 5 g. FeSi	365	200	2 da.	Lead	—	—	—
1 g. ZnO 1 g. SiO_2 or 5 g. FeSi	365	200	2 da. 3 da.	Willemite Zn_2SiO_4	1.70– 1.71	Needles and prisms	Moderately biref. S. G. = 4.2
300 mg. $Mn(OH)_2$ 1 g. SiO_2 or 200 mg. $Mn(OH)_2$ + 5 g. FeSi	365	200	2 da.	Tephroite Mn_2SiO_4	1.77– 1.79	Roundish grains or plates	Soluble in cold 2 N HCl S. G. = 3.35
100 mg. MgO 1 g. SiO_2 or 5 g. FeSi	365 380	200 250	2 da. 2 da.	Antigorite and Clinoenstatite	1.56 1.63– 1.64	Grains Needles	Insol. acids; greasy feel Insol. acids Ext. = 35°
CaO : MgO = 1 : 1 & 1 : 3 5 g. FeSi	395	300	3 da.	Both expts. produced Diopside	1.67– 1.69		Ext. angle = 39° Insol. acids

1931 116 VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B.: The pneumatolytic synthesis of silicates, II, *Rec. trav. chim.*, **50**, 989–96.

Another simple silicate was prepared in the same manner as in the earlier work (115):

(1) 500 mg. of CdO were placed in the upper crucible and 1 g. of amorphous silica in the lower. Treatment was for 2 days at 365° C. and 200 atmospheres of steam pressure.

(2) 500 mg. of CdO in the upper crucible; 5 g. of FeSi in the lower. Treatment for 2 days at 395° and 300 atmospheres.

Both experiments gave **Cd_2SiO_4** in small, irregular, colorless plates and prisms that were moderately birefringent, with $n > 1.74$. Composition: SiO_2, 19.1%; CdO, 78.6%. (SiO_2 : CdO = 1 : 1.94.)

In beginning experiments to prepare the alkali aluminum silicates they tried treating $KAlO_2$ and $NaAlO_2$ with siliceous vapors, but the aluminates always crept out of the crucibles under the conditions of the experiments, and had to be abandoned in favor of the orthosilicates *kaliophilite* ($KAlSiO_4$) and *nepheline* ($NaAlSiO_4$). These minerals were prepared artificially from pure kaolin with K_2CO_3 and Na_2CO_3, respectively, and were placed in the upper crucible and amorphous silica was placed in the lower one.

The table at the end of the abstract shows the results of these experiments; also the results of other sets of experiments: (1) With natural leucite or analcite in the upper crucible and amorphous silica in the lower one; (2) with CaO or MgO in the upper crucible and FeSi in the lower one, and using a partial pressure of CO_2 with the water; and (3) with CaO in the upper crucible and WO_3 or MoO_3 in the lower crucible instead of the silica. TiO_2 and SnO_2 used instead of silica in the lower crucible gave completely negative results.

A considerable solution of **copper** was found at 415° C. and 300 atmospheres, indicated by the formation of well-defined crystals near the top of the autoclave. Slight solution of silver was found, but none of CaF_2.

It is to be noticed that the partial pressure of CO_2 prevented the formation of wollastonite and clinoenstatite, under conditions otherwise identical to those under which they were obtained.

The formation of anhydrous **leucite** as an intermediate product between *kaliophilite* and **orthoclase,** but of hydrous **analcite** in the soda series is in harmony with the occurrence of these minerals in nature, where leucite and analcite, not leucite and jadeite, occur as equivalent constituents of intermediate rocks.

Photomicrographs of cadmium orthosilicate, skeletal leucite, orthoclase, analcite, and albite are given.

TABLE SUMMARIZING THE RESULTS; DESCRIPTIONS OF PRODUCTS (116).

Materials Used	T.(°C.)	P.(atm.)	Time	Product(s)	Indices	Form	Other Properties

TABLE SUMMARIZING THE RESULTS; DESCRIPTIONS OF PRODUCTS (116).

Materials Used	T.(°C.)	P.(atm.)	Time	Product(s)	Indices	Form	Other Properties
700 mg. kalioph. 500 mg. silica	395	300	3 da.	Leucite	1.510	Hexagonal or octagonal plates 20–60 μ	Very slight birefringence. Brittle. HCl leaves skeleton of amorphous SiO_2
700 mg. kalioph. 500 mg. SiO_2	As above for 3 days, then contents of upper crucible stirred to remove crust, 500 mg. of SiO_2 added to lower crucible; heating continued under same conditions for 5 days more			Leucite	1.510	Hexagonal or octagonal plates 20–60 μ	Very slight birefringence. Brittle. HCl leaves skeleton of amorphous SiO_2
				Orthoclase	1.514–1.530		Insoluble in HCl Moderately birefringent
1 g. leucite 1 g. silica	395	300	3 da.	Orthoclase	1.514–1.530		Insoluble in HCl Moderately birefringent S. G. = 2.3
1 g. nepheline $\frac{1}{2}$ g. silica	395	300	3 da.	Analcite	1.49	Tabular plates	Insoluble in dilute acetic acid
1 g. nepheline 2 g. silica	380	275	7 da.	Analcite Albite	1.47 1.53	Tabular plates Oblique prisms	Insoluble in dilute acetic acid Insoluble in HCl
1 g. nat. anal. 1 g. SiO_2	395	300	3 da.	Albite	1.53	Oblique prisms	Ext. = 20° S. G. = 2.3
300 mg. CaO 5 g. FeSi	365	200 H_2O 100 CO_2	2 da.	$CaCO_3$			Soluble in dilute acetic acid. Strong birefringence
200 mg. MgO 5 g. FeSi	365	200 H_2O 100 CO_2	2 da.	$MgCO_3$ + Antigorite			
$\frac{1}{2}$ g. CaO 1 g. WO_3	380	275	3 da.	Scheelite $CaWO_4$	1.74	Irreg.	Feebly birefringent. WO_3 : CaO = 1 : 1.08
1 g. CaO 1 g. MoO_3	395	300	3 da.	Powellite $CaMoO_4$			

1932 **117** VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B.: The isotherms of water from 350–480° C. and for pressures up to 600 kg./cm^2., *Rec. trav. chim.*, **51**, 708–14.

Work preliminary to the quantitative determination of the solubility of silica in super-critical steam (147), giving the data indicated in the title.

1932 **118** MOREY, GEORGE W.: The volatility of silica with steam, *Trans. Am. Geophys. Union*, **13**th Annual Meeting, 269–70.

Morey questions the work of van Nieuwenburg and Blumendal (111) on the grounds that under the reported conditions of temperature and pressure their crucibles would have been filled with liquid water before the critical temperature was reached; hence much, if not all, of the transport may have been produced by liquid rather than by super-critical steam.

He repeated their experiments, varying the conditions just enough so that all of the water in the bomb would volatilize before the liquid came above the level of the lower crucible. He obtained weights that, although measurable, were not of the same order of magnitude as those obtained by van Nieuwenburg and Blumendal (.0001 to .0004 g. after runs of 5 to 24 days). Morey concluded that the difference was due to the use of a larger amount of water by the earlier experimenters, possibly allowing the transfer to take place in the liquid phase. He indicated that his experiments did not exclude the possibility of some transport through the vapor phase. He found the time of duration of the experiments to be without appreciable effect.

1932 **119** BADGER, A. E., AND ALLY, A.: Note on the formation of kaolin minerals from feldspar, *J. Geol.*, **40**, 745–7.

Five per cent hydrofluoric acid with *potassium feldspar* for 24 hours at 225° C. produced a substance whose X-ray pattern duplicated that of **kaolinite** save for two lines, and contained two extra lines. The lines were diffuse and the product may have been either **kaolinite** or **dickite.** No X-ray diagrams are given, but a table of the spacing and intensities of the lines of a diagram from natural kaolin and of one from the material produced by the action of hydrofluoric acid on potassium feldspar is included.

No kaolin was produced by the action of H_2CO_3 on *potassium feldspar* in 156 hours at 60° and under a pressure of 1800 pounds per square inch.

1932 **120** KARL, ADRIEN: Sur la willémite synthétique, *Compt. rend.*, **194**, 1743–5.

Crystalline **willemite** was prepared by heating finely pulverized silica, NaCl, and an excess of $ZnCl_2$ in water vapor at 600° C.

1932 **121**

1932 **122**

The $ZnCl_2$ distilled off so that at the end of an hour the entire charge was solid. An upper crust was composed of crystals that were visible to the naked eye; the lower part of the charge was microcrystalline. The soluble salts were leached with water and the zinc oxychloride was removed with very dilute HCl.

Fluorescence of natural willemite is supposed to be due to minute quantities of impurities, especially nickel, copper, and iron. Karl prepared some very pure $Zn(NO_3)_2$ by crystallizing it 400 times into 10 fractions. Pure silica was prepared from $SiCl_4$ that had been purified by numerous distillations; the NaCl was also purified by numerous crystallizations. None of these materials showed any fluorescence when treated with cathode rays. However, the **willemite** prepared from them showed a violet fluorescence. A vivid emerald green fluorescence was produced by the action of cathode rays on artificial **willemite** containing .001–.002% nickel. That containing .0005–.002% copper showed a blue-green fluorescence the intensity of which varied with the intensity of the cathode rays. A mixture of .001% nickel and .00025% copper in the synthetic mineral produced a very brilliant green fluorescence that gave a spectroscopic band like that of natural willemite.

1932 **121** NAGAI, S.: Hydrothermale Synthesen von Calciumsilikaten, I, *Zeit. anorg. Chem.*, **206**, 177–95.

Nagai heated mixtures of CaO and *quartz* with ratios $5CaO : 1SiO_2$ to $1CaO : 5SiO_2$ at temperatures from 132° to 213° C., under steam pressures from 3.5 kg./cm.² to 20 kg./cm². On the basis of chemical analysis alone he obtained ratios of combined CaO to combined SiO_2 of various values, all of which are reduced to the simple ratios 2 : 1, 1 : 1, and 3 : 2, in spite of the fact that some of them are as far off from these ratios as 1.31 : 1 and 3.37 : 2.

It is not considered worthwhile to give the results of these experiments in detail, since neither optical nor X-ray data are given.

Nagai says that these " reactions " take place some 300° lower in the presence of steam at one atmosphere than in dry syntheses.

1932 **122** NAGAI, S.: Hydrothermale Synthesen von Calciumsilikaten, II, *Zeit. anorg. Chem.*, **207**, 321–39.

Nagai continued his experiments, using $CaCO_3$ in place of CaO in some of the runs. The results were similar to those of the runs with CaO in which the molecular ratios were the same, there being slight differences in the times of reaction, and in the $CaO : SiO_2$ ratios. Anhydrous silicates were formed in one atmosphere of steam, but under greater pressures several hydrates appeared to be formed:

TABLE OF EXPERIMENTS SHOWING THE PREPARATION OF THE HYDROUS CALCIUM SILICATES.

Exp. No.	$CaO : SiO_2$ Used	P(kg./cm.²)	Temp.	Time	$CaO : SiO_2 : H_2O$	Product	Simplified Ratio; Name
6	1 : 1	10	180	6 da.	1.01 : 1 : 0.273		1 : 1 : 0.25 = Xonotlite, which predominates in these
21	1 : 1	10	180	6 da.	1.03 : 1 : 0.276		3 exps. There was some afwillite in each case
12	1 : 1	15	200	6 da.	1.09 : 1 : 0.281		
17	3 : 2	5	153	6 da.	3.31 : 2 : 7.98	Afwillite	
16	2 : 1	5	153	6 da.	3.13 : 2 : 8.36	3 : 2 : 8	
4	2 : 1	10	180	6 da.	3.33 : 2 : 1.02	3 : 2 : 1—Unknown in nature	
10	2 : 1	15	200	6 da.	3.09 : 2 : 0.93	Some afwillite in each case	
39	3 : 1	10	180	6 da.	2.03 : 1 : 0.95	2 : 1 : 1—Hillebrandite. Some afwillite in each case	
49	5 : 1	5	153	6 da.	2.04 : 1 : 1.09		

Xonotlite—$CaO : SiO_2 : .25H_2O$ (Dana-Ford—5 : 5 : 1).
Afwillite—$3CaO : 2SiO_2 : 8H_2O$ (Dana-Ford—3 : 2 : 3).
Hillebrandite—$2CaO : SiO_2 : H_2O$ (Dana-Ford—2 : 1 : 1).
New compound (?)—$3CaO : 2SiO_2 : H_2O$.

It is stated that these compounds were identified by optical and X-ray data and that they were compared with the corresponding natural minerals microscopically. The table below summarizes the experiments in which these hydrous minerals were produced. The optical properties are not given, nor are there any X-ray diagrams or tables. As in the first article no data except chemical are mentioned for the anhydrous silicates, so it is not considered worth while to outline here the many experiments performed.

1932 **123** NOLL, W.: Hydrothermalsynthese von Muskovit, *Naturwiss.*, **20**, 283.

A preliminary note giving the conditions of the experiment and stating that the product was identified by means of X-rays. Noll prepared a colloidal adsorption "compound" of composition $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot xH_2O$ by adsorption of K^+ in a "Schwarz and Brenner" gel (96) with the ratio $Al_2O_3 : SiO_2 : H_2O = 1 : 2 : 2$. This material treated for 5 days at 300° C. gave **muscovite.** Noll thinks that this formation of fine grained muscovite corresponds to natural sericitization of allophanous material in sediments. For details see (124).

1932 **124** NOLL, W.: Hydrothermale Synthese des Muscovits. Ein Beitrag zur Frage Serizitbildung in Tonschiefern, *Nach. Gesell. Wiss. Göttingen, Math.-Physik. Kl.*, **1932**, 122–34.

Noll prepared a colloidal adsorption material of the composition $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot xH_2O$, by allowing a gel like those prepared by Schwarz and Brenner (96) to take up K^+. He placed some of this material in a platinum crucible in a steel bomb of 650 cc. capacity, heated the bomb to a given temperature in 5 to 6 hours, then kept the temperature constant for 5 days, after which he allowed the bomb to cool slowly.

The following experiments are recorded:

	In crucible:		In bomb:				
Exp. No.	Preparat. No. 122 [1]	H_2O cc.	cc. of H_2O	Temp. °C.	Pres. Atm.	Time, Days	Result
I	150 mg.	5	150	300	90	5	Muscovite
III	150 mg.	5	100	250	40	5½	Muscovite
IV	120 mg.	4	100	225	26	5	Less muscovite
II	150 mg.	5	100	200	16	5	Amorphous

[1] Preparation No. 122 was an adsorption gel with the following composition: 35.08% SiO_2, 30.56% Al_2O_3, 10.46% K_2O, and 24.12% H_2O. This composition corresponds to $2.03SiO_2 : 1.00Al_2O_3 : .36K_2O$, aq.

Discussion of the experiments:

I. The flakes were too small for microscopic description, but a 1600-fold magnification shows birefringent flakes ranging from .3 to 2μ long and not quite so wide, with the higher index apparently parallel to the greater dimension. All of the lines of the X-ray diagram correspond to **muscovite,** showing the absence of any other crystalline compound. The diagrams were compared with those from kaolin and pyrophyllite, both of which were definitely different from the pattern produced by the synthetic material. The intensities of the different lines do not agree with those of the natural material as well as do the positions, but this difference is ascribed to the fineness of division of the artificial preparation. No X-ray diagrams are given in the paper, but there are tables of the spacing and intensities of the lines for natural muscovite and for some of the preparations.

III. Practically identical with I.

IV. The X-ray diagram from the product showed only the stronger lines shown by the products of I and III and the lines are broader and more indefinite, probably because the material is in still finer particles. No lines characteristic of other compounds were noted.

II. Amorphous.

Noll concludes that 225° C. is the lowest temperature for the formation of **sericite** under the conditions of the experiments, in 5 days, but he realizes that this does not mean that sericite cannot form in nature at lower temperatures where great lengths of time are available. There was a considerable difference in the rate of formation of sericite at 250° and 225°.

1933 **127**

1933 **128**

1932 **125** NOLL, W.: Synthese des Kaolins, *Naturwiss.*, **20**, 366; also *Fort. Min. Krist. Petr.*, **17**, 1933, 65–6.

This is a preliminary notice outlining the conditions under which kaolin was prepared:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow[\text{or at } 300^\circ \text{ C. and } 90 \text{ atm.}]{5 \text{ days at } 250^\circ \text{ C. and } 40 \text{ atm.}} \text{“undoubted” } \textbf{kaolinite.}$$

For the details of these experiments see (135).

The product was identified by its X-ray pattern. Noll believes that this manner of preparation of **kaolinite** corresponds to its hydrothermal formation in nature.

1932 **126** GOLDSCHMIDT, V. M.: Neue Wege und Gesichtpunkte bei der Synthese von Mineralen und Gesteinen, *Naturwiss.*, **20**, 337–40.

A general review and partial bibliography. The following pertinent observations are made:

(1) A mineral must be shown to have the proper structure as well as the appropriate chemical composition before it may be considered to have been synthesized.

(2) One of the great difficulties with hydrothermal syntheses is that the crystals are too small for microscopic determination.

(3) A present need is to study the hydrothermal alteration of good crystals of artificial minerals of accurately known composition; for example, the alteration of plagioclase and pyroxene to sassurite and uralite, respectively. The minerals should not be powdered and the products should be studied by means of X-rays.

1933 **127** SCHEUMANN, K. H.: Über Hornblendesynthesen bei niederen Drucken, *Fort. Min. Krist. Petr.*, **17**. 69.

A short note stating that **hornblende** was produced at various pressures in the presence of mineralizers. The best results were obtained with fluorine-bearing compounds when water was also present to act as an ionizing agent. In one such experiment at atmospheric pressure crystals of **hornblende** 4 mm. long were formed. They were identified by their optical properties and X-ray diagrams, but neither the optical properties nor diagrams are given in the abstract.

1933 **128** DITTLER, E.: Zur Frage der Kaolinbildung, *Zeit. anorg. Chem.*, **211**, 33–40.

Earlier work by Schwarz and others (96), (99) and Noll (124), (125) is cited. Also the following: Sh. Khasai (Die wasserhaltigen Aluminiumsilikate, Diss., München, 1896) obtained a precipitate, $Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$, by reaction of an $Al(OH)_3$ sol that contained chloride with silicic acid sols that had .8 g. to 1.8 g. of SiO_2 per 100 cc. B. Aarino (*Zent. f. Min.*, 1908, p. 622) by using hydrosols of aluminum hydroxide and silicic acid obtained precipitates ranging from $Al_2O_3 : 0.73SiO_2$ to $Al_2O_3 : 14.63SiO_2$. The sols contained abundant electrolytes.

Dittler carefully prepared sols of $Al(OH)_3$ and silicic acid and let them react under closely controlled pH conditions, with values between 4.8 and 4.9, within the best range prescribed by Schwarz for the formation of " prokaolin " with an almost constant ratio of $Al_2O_3 : SiO_2 = 1 : 2$. However, Dittler obtained precipitates with practically the same ratios as the mixtures with which he started, varying from $Al_2O_3 : 2SiO_2$ to $Al_2O_3 : 10SiO_2$.

He concludes that the nearly constant ratio, 1 : 2, obtained by Schwarz and Walcker (99), although they started with a ratio of 1 : 6, was due to true chemical action between electrolytes and not to flocculation of colloids.

1933 **129** GILLS, J.: Verluchtiging van SiO_2 en van koper in stoom, *Natuurwetensch. Tijds.*, **15**, 153–4. (From *Min. Ab.* **5**, p. 446.)

Confirmed the earlier work of van Nieuwenburg and Blumendal on the volatility of silica in super-critical steam, using a similar apparatus in which ZnO was placed in one crucible and SiO_2 in another, and the two were placed near the top of a copper tube and the tube autoclaved under 300 atmospheres of steam. The copper tube was 50 cm. long and the water placed in the bottom of it was only 5–10 cm. deep, so there was no possibility that the crucibles would be flooded before the critical temperature was reached. Transport of silica was indicated by the formation of **willemite** in the crucible containing ZnO. Some volatility of the copper was noted.

1933 **130** GREIG, J. W., MERWIN, H. E., AND SHEPHERD, E. S.: Notes on the volatile transport of silica, *Am. Jour. Sci.*, (5) **25**, 61–73.

Wrapped powders or small fragments of rocks ranging in composition from *obsidian* to *basalt* in platinum foil and heated at 600–1200° C. in sealed silica tubes that had been evacuated to .02 mm. of mercury. Deposits of **cristobalite** formed on the foil in such positions that transfer must have been effected through the vapor phase. There was no noticeable transfer below 700°. Above that temperature, although no quantitative measurements were made, it was evident that the rate of formation of the deposits was faster at higher temperatures. No deposits formed when the rocks had been degassed at high temperatures before the experiment, indicating that the volatile materials contained in the rocks were essential to the transport.

Water alone effected transfer of silica, " at an important rate," from the sides of the tubes to arched pieces of platinum foil so arranged that they did not touch the sides where the deposits were formed. Therefore, the transfer must have been through the vapor phase. Other experiments showed no indication of the formation of volatile compounds of silicon by means of which the transfer might have been effected.

1933 **131** SCHEUMANN, K. H., AND LÜDKE, W.: Über Hornblendesynthesen bei niederen Drucken, *Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math.-phys. Klasse*, **85**, 273–8. Also LÜDKE, WERNER: Methodisches zur Synthese von Silikaten mit leichtflüchtigen Substanzen unter stationären Bedingungen, *Fort. Min. Krist. Petr.*, **18**, 29–31, 1934.

Amphibole, mica, and other minerals containing OH and F are usually formed at high pressures. However, their occurrence on crater rims and in open volcanic fissures indicates that they may also form at low pressures, if the proper mineralizers are present.

In the laboratory study water and various compounds of fluorine were the chief mineralizers used.

In the experiments mixtures with tremolite-like compositions were used. The components (silicofluorides, bicarbonates, silica gel, etc.) were pressed into elongate pastilles and heated in an oven below 900° C. This treatment produced some fine needles of **hornblende.** The samples were then treated under strongly reduced pressure, later at 2–3 atmospheres, and finally in a free gas stream at one atmosphere. This treatment presumably produced better fibers, although this is not specifically stated. Parallel experiments in pressure bombs gave similar, but poorer, results.

The products were studied microscopically and by means of X-rays. In the paper by Scheumann and Lüdke X-ray diagrams for two of the preparations are reproduced and a diagram for natural tremolite is given for comparison. From these photographs line diagrams are drawn for one of the preparations and for the natural tremolite.

In both papers a chemical analysis of one of these preparations is given, and one of another preparation for which no X-ray diagram is shown:

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	H_2O	F	Sum
61.10	0.43	trace	18.75	6.62	12.07	0.64	1.90	101.51
61.48	6.60	trace	18.98	—	8.71	3.96	1.36	101.09

For these two preparations $RO : SiO_2 = 1.017 : 0.92$ and $1.02 : 0.97$, respectively, and the specific gravities are 2.676 and 2.691. $n = 1.595$ and $Z \wedge c = 18–19°$ for both of them. An iron-containing hornblende gave $n = 1.635$; specific gravity = 2.915; $Z \wedge c = 20–22°$. A picture of a group of the synthetic **hornblende** fibers is given in the first paper.

Neither compositions of the mixtures used nor the conditions of the experiments are given, because the process is said to be tied up with Germany's problem of supplies of raw material, especially the production of asbestos, and to be applicable to the hydrothermal and pneumatolytic synthesis of other minerals, such as **mica, garnet,** and **tourmaline.** The results are said to be reproducible with certainty.

1933 SCHWARZ, R.: Künstliche Umwandlung von Feldspat in Kaolin,
132 *Naturwiss.*, **21**, 252.

Reviews the theory of the formation of **"prokaolin"** (see 99) from feldspar and its ultimate change to kaolin, and says that he has now prepared kaolinite from *feldspar* in the laboratory by treating it with 0.5 N to 1.0 N HCl or H_2SO_4 at 300° C. for 250

hours. The product was identified by its dehydration curve, which was practically identical with that of kaolinite formed from synthetic prokaolin. X-ray determination by Goldschmidt, but no diagrams or tables are given in the paper. No dehydration curves are reproduced and no optical data given.

Leucite gives **kaolinite** in the same manner. This supports the theory that feldspar first breaks up into primary decomposition products, some of which re-combine to form kaolin, because it shows that the feldspar composition is not necessary to form kaolin; it is only necessary to have a mineral that can furnish the necessary primary decomposition products.

Kaolin may originate in a similar way in nature, by the action of superheated vapors on feldspar during the igneous cycle.

1933 SCHWARZ, R., AND TRAGESER, G.: Über die künstliche Umwand-
133 lung von Feldspat in Kaolin, *Zeit. anorg. Chem.*, **215**, 190–200.

Using steel bombs, with volumes of 40 and 120 cc., and heated in electric furnaces, they tried the action of various solutions on *potassium feldspar*, *anorthite*, *leucite*, and *kaolin*. The following table gives a summary of the results:

Mineral Used	Solution	Time, Hrs.	Temp. °C.	Product; Identification; Remarks
K-feldspar	1 N HCl	250	330	Kaolinite; dehydration curve, X-ray pattern, index of refraction, form of flakes
"	N/2 HCl	115	320	Kaolinite; dehydration curve, X-ray pattern, index of refraction, form of flakes
"	"		180 250	No kaolinite, but a residue with Al_2O_3 : SiO_2 = 1 : 7 to 1 : 8.6
Anorthite	"	60	340	Kaolinite; dehydration curve (only?). Contains 13.2% H_2O; theoretical content is 13.9%
Leucite	"	60	320	Kaolinite; dehydration curve (only?). 110 atm.
Feldspar	2 N, N/2, and N/4 H_2SO_4		300	No kaolinite; watery residue containing very little alkalis or alumina
"	2 N H_2F_2		180 210 235 320	No kaolinite. This result is contrasted with that of Badger & Ally (116) and attention is called to the fact that S. & T. found natural kaolin to be decomposed by hydrofluoric acid under similar conditions. (See below, in this table.)
"	H_2CO_3	250	320	No kaolinite. 190 atm.
Kaolin (Nat.)	N/2 HCl	150	320	Increases water content from 12.8% to 14.4%.. Shape of dehydration curve is unchanged[1]
"	1 N HCl		320	"Loosens" a part of the water, as indicated by a change in the dehydration curve[2]
"	N/2 HCl		220	Kaolin decomposed; no new mineral formed

(*Table continued on next page*)

Mineral Used	Solution	Time, Hrs.	Temp. °C.	Product; Identification; Remarks
Kaolin (Nat.)	1 N H_2SO_4	90	280	Mass no longer plastic; no kaolinite lines in X-ray pattern. Loses 24.2% water on heating; 16% of which comes off above 460°
"	2 N H_2F_2		310	Kaolin decomposed; fluorine-containing residue with 27% water (Above 110°)
"	N/2 H_2F_2		150	Kaolin decomposed; fluorine-containing residue with 16% water (Above 110°)

[1] This increase in the water content may indicate that some allophanous material in the kaolin is hydrated to kaolinite under the conditions of the experiment.

[2] This experiment, together with the one above, indicates that the most favorable conditions for kaolinite formation are with N/2 HCl at 320° C.

Dehydration curves are given for the preparations, but no X-ray diagrams, tables of lines, or optical data.

1934 **134** NOLL, W.: Zur genetischen Deutung der hydrothermalen Kaolinsynthese, *Centr. Min.*, **1934**, 80–4.

A very brief summary of the ideas concerning the formation of kaolin:

Rössler (1902)—Pneumatolytic.

Stahl (1912)—High temperature hydrothermal.

Ross and Kerr (1931)—Low temperature formation.

Noll reviews his earlier work and that of SCHWARZ and BRENNER and says that he has now prepared **kaolinite** directly from a mixture of hydrous alumina and silica with a ratio $Al_2O_3 : 6SiO_2$ at 300° C.

The fact that **kaolinite** was formed at 320° in the presence of N/2 HCl, but decomposed by it at 220°, should not be taken as evidence that kaolin cannot form at 200°, or even at lower temperatures, because a change in the acid concentration might allow the formation of kaolin at lower temperatures, especially if sufficient time is allowed.

1934 **135** NOLL, W.: Hydrothermale Synthese des Kaolins, *Min. petr. Mitt.*, **45**, 175–90.

A gel of **prokaolin** was prepared by reaction of $AlCl_3$ and Na_2SiO_3 solutions. Charges of 150 mg. each were mixed with 4 or 5 cc. of water, placed in a platinum crucible, which was in turn placed in a bomb of 650 cc. volume with 100 cc. of water. The bomb was heated to a given temperature in 5 hours, held at that temperature for 5 days, and then cooled slowly. Charges held at 300° C. (90 atmospheres) and 250° (40 atmospheres) produced **kaolinite,** while those held at 205° (18 atmospheres) and 160° (6 atmospheres) failed to show it.

The **kaolinite** was identified by X-ray diagrams, water content,

dehydration curves, solubility of the alumina in HCl, and the index of refraction. Debye-Scherrer diagrams for natural and synthetic kaolin are reproduced, and the lines of these diagrams are listed and described in tables. The index of the artificial product is 1.5505–1.568.

1934 136 VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B.: On the volatility of silica in super-critical steam, *Rec. trav. chim.*, **53**, 476.

An answer to Morey's criticism (118), acknowledging that in their experiments the conditions were such as to permit the liquid phase to enter the crucibles. They admit that this may have had an effect on the magnitude of the results, but believe that it is not the major factor because: (1) They repeated Morey's experiments and found that the formation of **willemite** took place just as well when the amount of water was too small to reach the level of the crucibles before the critical temperature was reached. No data on the amount of transport are given. (2) The amount of transport is a function of time, until equilibrium is reached after about five hours.

It is explained that the losses in weight do not represent real solubilities, because they are partly due to sublimation towards the somewhat colder top of the autoclave. (As well as in part to the removal of the silica from the vapor phase by the ZnO.)

1934 137 VIGFUSSON, V. A., BATES, G. N., AND THORVALDSON, T.: Hydrothermal synthesis of calcium hydrosilicates, *Can. Jour. Research*, **11**, 520–9.

Cement mortar made of quartz sand and cement high in tricalcium silicate when treated with saturated steam under pressure at 150° produced crystalline **calcium hydroxide** and an orthorhombic **hydrous calcium silicate** that could not be identified with any known calcium silicate hydrate. Continued steaming caused the complete disappearance of the calcium hydroxide. See (110) for the optical and some of the chemical properties of the silicate. The crystals were slowly decomposed by solutions of normal alkali carbonates, with the formation of **calcite** on the surfaces attacked, and decomposed by sulfuric acid with the formation of **gypsum.**

When it was proved that these crystals were a **hydrous calcium silicate** (thought to be $2CaO \cdot SiO_2 \cdot H_2O$), attempts were made to prepare the crystals from pure materials. Treatment of a 1 : 10 mixture of CaO and quartz for 48 hours at 150° C. produced large quantities of the crystals, and some crystalline $Ca(OH)_2$ remained after that time. The same compound was formed by hydrothermal treatment of mixtures of di- and tricalcium silicates and quartz.

The following sets of experiments are recorded:

1. CaO was mixed with five times its weight of *quartz* sand and to the mixture was added enough water to form a thick paste. It was then autoclaved in saturated steam at 170° C. for 2 weeks. The product was the orthorhombic **hydrous calcium silicate.**

2. *Quartz* crystals and *fused silica* plates were suspended in saturated *lime water* in silver containers, in the bottom of which was placed an excess of lime. After being autoclaved for 7 to 14 days at 170° C. the surfaces of the crystals and plates were studded with orthorhombic crystals that were up to .5 mm. in length. In some of the runs **needle-like crystals** appeared on the solid $Ca(OH)_2$ in the bottom of the vessel. When nickel-plated containers were used the silica plates were covered with laths and fine needles and large laths formed on the inner walls of the vessels. In some of the experiments with the silica plates a film of very finely divided crystalline material of low birefringence, with an occasional lath, was formed on the surfaces of the plates. Two analyses of these films agreed very closely and gave a mean value of $0.86CaO \cdot SiO_2 \cdot 0.56H_2O$. The X-ray pattern of this material was entirely different from those of the laths or needles.

Three analyses of the orthorhombic plates produced in these experiments averaged $1.07CaO \cdot SiO_2 \cdot 1.24H_2O$. The crystals were brittle, with a hardness of 5; prismatic cleavage; Z parallel to the direction taken as crystallographic *c*; axial plane parallel to (100); cruciform twins and radial growths observed.

3. Mixtures of CaO and silica gel with $CaO : SiO_2 = 4 : 1$ when given the hydrothermal treatment described above for CaO and quartz sand, gave **needles** whose X-ray diffraction pattern and optical properties differed clearly from those of the lath-like plates described above. Two analyses gave a mean value of $2.15CaO \cdot SiO_2 \cdot 1.42H_2O$. Despite this value for H_2O the needles are considered to be another 2 : 1 : 1 compound with a different structure, but the possibility is suggested that there may be more than one molecule of water in the structure. The needles usually formed radial clusters; weakly birefringent; parallel extinction; positive elongation; mean index = 1.597 ± .003, indicating that the crystals may be **foshagite,** since the indices for hillebrandite are considerably higher than this value.

A table of the spacings and intensities of lines of the X-ray diagrams of (1) the crystals obtained from steamed cement, (2) those prepared from quartz crystals and silica plates in lime water, (3) the needles prepared from CaO and silica gel, (4) natural hillebrandite, and (5) crystalline $Ca(OH)_2$, is included, and these data are also presented graphically in line diagrams. No actual

pictures of X-ray diffraction patterns are reproduced. Four photomicrographs and fourteen drawings of the platy orthorhombic crystals are given.

The diagrams from the crystals from cement and from the quartz and lime water are similar enough to suggest that the two may be identical. The diagram from the needles is entirely different from those of the plates. It shows some similarity to the one from **hillebrandite,** but is in general different. The diagram from $Ca(OH)_2$ is entirely different from the others. No suggestion is made that any of the products might be afwillite, so no X-ray diagram of this mineral is given.

1935 EWELL, R. H., AND INSLEY, H.: Hydrothermal synthesis of kaolin-
138 ite, dickite, beidellite, and nontronite, *J. Res. U. S. Bur. St.*, **15**, 173–86; RP819.

Four of the clay minerals were synthesized in a bomb of the type used by Morey (89). (1) **Kaolinite,** from coprecipitated Al_2O_3-SiO_2 gels and mixtures of alumina and silica with water at 310° C. (2) **Dickite,** from the gels at 350° and 365°. (3) **Beidellite,** from mixtures of silica and alumina at 350° and 390°; from coprecipitated gels and from kaolin at 390°. (4) **Nontronite,** from a coprecipitated gel, $Fe_2O_3 \cdot 2SiO_2$ at 350°. Re-examination of some of the charges after the results had been published showed **pyrophyllite** in at least one of the 390° runs.[1]

The following table gives the conditions and results of most of the experiments:

No.	Material	Time, Days	Temp. °C.	Pres. Atm.	Products
1	$Al_2O_3 \cdot 2SiO_2$ gel	300	Room	1	Amorphous
2	"	300	Room	1	Amorphous
3	"	100	95	1	Amorphous
4	"	100	95	1	Amorphous
5	"	11	250	39	Weak showing of kaolinite
6	"	7	310	97	Kaolinite
7	"	7	345	157	Weak dickite
8	"	11	345	157	Dickite
9	"	10	365	202	Dickite
10	$Al_2O_3 \cdot 4SiO_2$ gel	10	350	167	Dickite
11	$Al_2O_3 \cdot SiO_2$ gel	8	350	167	Dickite and boehmite
12	$2Al_2O_3 \cdot SiO_2$ gel	10	350	167	Boehmite
13	Al_2O_3 gel + SiO_2 gel (mixed)	10	310	97	Kaolinite
14	Al_2O_3 gel + SiO_2 gel (mixed)	12	350	167	Beidellite
15	Al_2O_3 gel + SiO_2 glass	12	350	167	Beidellite and faint boehmite
16	γ-Al_2O_3 + SiO_2 gel	18	350	167	Beidellite

[1] Personal communication from H. Insley.

(*Table continued on next page*)

No.	Material	Time, Days	Temp. °C.	Pres. Atm.	Products
17	γ-Al_2O_3 + SiO_2 glass	18	350	167	Beidellite
18	Boehmite + $3SiO_2$ gel	9	350	167	Boehmite and beidellite
19	Boehmite + $3SiO_2$ glass	9	350	167	Boehmite and beidellite
20	Al_2O_3 gel + $2SiO_2$ gel	10	390	260	Beidellite
21	γ-Al_2O_3 + $2SiO_2$ gel	10	390	260	Beidellite
22	$Al_2O_3 \cdot 2SiO_2$ gel	14	390	260	Beidellite
23	Zettlitz kaolin	14	390	260	Beidellite
24	Al_2O_3	5	350	167	Boehmite
25	γ-Al_2O_3	5	350	167	Boehmite
26	Boehmite	5	350	167	No change
27	SiO_2 gel	5	350	167	Cristobalite
28	SiO_2 glass	10	350	167	No change
	$Fe_2O_3 \cdot 2SiO_2$ gel	6	350	167	Hematite and nontronite

Andalusite, kyanite, sillimanite, mullite, pyrophyllite, and *orthoclase* were heated in the bomb for 10 days each at 350° C., but no change was observed in any of them.

A series of experiments was performed to study the mechanism of formation of the **beidellite** (Table 4, p. 182 of the original). They used a small platinum capsule with the lid wired on tightly to prevent convection currents, placed alumina gel in the capsule and silica gel outside, and vice versa, and made runs of various lengths at 355° and 385°. The results showed that the silica was dissolved and carried to the alumina, with which it reacted in situ, both below and above the critical temperature. When the bomb was cooled as soon as the critical temperature had been passed there had been no determinable transport of silica, but when the temperature was held at 385° for 12 days there was a considerable transport, indicating that it had been effected through the vapor phase.

Experiments with soda-free gels [1] failed to produce beidellite, indicating that soda is either necessary for its formation, or that its presence speeds up the formation enormously. A similar relation may hold for kaolin and dickite, but no coprecipitated gels free from soda were used to check that possibility.

Identification was by means of X-ray patterns. One pattern for each synthetic mineral (two for **beidellite**) and patterns from the natural minerals are given. The correspondence is very good, except in the case of **nontronite,** which showed, in addition to all of the lines of the natural material, several extra ones that do not correspond to any known form of iron oxide or silica.

No detailed optical study of the products could be made, because they were too fine grained. However, each charge was

[1] It was found late in the investigation that all of the gels involving the use of either NaOH or Na_2SiO_3 in their preparation contained small amounts of soda.

examined under the microscope to make sure that the optical properties that could be determined, principally the mean index and apparent birefringence, were consistent with the results of the X-ray examination. In the case of **nontronite** the microscope showed two different phases, in sub-equal amounts: (1) Small needles and plates with $\gamma = 1.63$; $\alpha = 1.60$; positive elongation and parallel extinction. (2) Larger masses of weakly birefringent green material with no extinction position. Chemical analysis of the material after drying at 110° gave the following ratio: $Fe_2O_3 : 3.43SiO_2 : 1.04H_2O$.

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The stability ranges of kaolinite, dickite, beidellite, (and pyrophyllite?) probably occur in that order with increasing temperature.

1935 **139** HITCHEN, C. S.: A method for the experimental investigation of hydrothermal solutions, with notes on its application to the solubility of silica, *Trans. Inst. Min. Met.*, **44th Session,** 255–336. (Printed 1936.)

Devised an autoclave fitted with a filter cup and needle valve by means of which samples of solution could be withdrawn at any desired temperature and pressure. A mixture of 5 g. of amorphous silica and 900 cc. of distilled water was heated in the pressure vessel at the desired temperature for 24–60 hours. A 100 cc. sample of the solution was then withdrawn into a platinum dish and analyzed for silica. Another sample was taken each time after keeping the temperature constant for 48–84 hours from the time of beginning, and the silica content compared with that of the first sample. Equilibrium was reached in about 24 hours at 150°; more time was required at lower temperatures; less, at higher.

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The results showed a definite increase in the solubility of silica with rising temperature; from .0493 part per 100 parts water at 128° to .2162 part per 100 at 336°. Fig. 11 is a graph showing the complete results of the study of the solubility of silica in pure water; the points for 25° and 90° are taken from the work of Lenher and Merrill (90). Gruner's results (112) are superposed on the same diagram for comparison.

Preliminary experiments were also performed to determine the influence of sodium metasilicate on the solubility of silica. 900 cc. of a 0.1 M solution of Na_2SiO_3 were used with 40 g. of amorphous silica. Over the range investigated, 127–280°, the solubility was considerably greater than with pure water, but the solubility decreased rapidly with increasing temperature. This decrease is ascribed tentatively to the breaking down of the polysilicates at the

higher temperatures. He apparently believes this to be a case of true solution, without considering the possibility of reactions in the system Na_2O-SiO_2-H_2O.

The bulk of the paper as printed, pages 280–336, is a very interesting discussion by a number of mining men and geologists. They point out a number of advantages of Hitchen's apparatus, point out difficulties in the path of further advance, and cite various applications to theoretical and practical problems.

1935 **140** NAGAI, S., AND SUZUKI, T.: Studies on products of hydrothermal reaction on clayey substances, I, *J. Soc. Chem. Ind., Japan*, **38**, Sup. Binding 371B–373B.

Six analyzed *clays* were autoclaved at 375° C. and 200 kg./cm.^{2} for four hours with no apparent change. The *clays* were then treated with 30% NaOH under pressures of 20–100 kg./cm.^{2} (temperatures not given) and the product analyzed after drying at 105°. The formation of a **zeolite,** $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, is assumed, although the analyses when recalculated to $Al_2O_3 = 1.00$ show as much variation as $1.26Na_2O$; $2.29SiO_2$; $1.46H_2O$. No optical or X-ray data are given.

This material, after base exchanging with $CaCl_2$ or $CaAc_2$, was " seen to contain some lime " and another compound, $CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, is supposed to have been formed, though not even chemical analyses are given to attempt to establish this formula.

1935 **141** NOLL, W.: Mineralbildung im System Al_2O_3-SiO_2-H_2O, *Neues Jahrb. Min. Geol.*, **Beil. Bd. 70,** 65–115.

In some of these new experiments the bomb mentioned in (135) was used (volume = 650 cc.), but in most of them two new bombs with a volume of 6 cc. each were used. A regulator held the temperature to about 1% of the desired value.

Silica gel and alumina gel were used in the experiments; the latter crystallized rapidly to **boehmite** and **bayerite** and, much more slowly, to **hydrargillite.** Most of the alumina was used in the form of *boehmite* and *bayerite*. When the two were used separately the only observable result was a difference in the rate of reaction, boehmite reacting more readily. This produced an apparent lowering of the temperature of reaction with boehmite, which may not have been real. The rate of cooling and the degree of filling of the bomb had little, if any, effect on the nature of the product.

The products were all cryptocrystalline when the temperature of the experiment was below 300° C., and mostly cryptocrystalline in the runs above 300°. The results are summarized in the following table:

Exp. No.	Temp. °C.	Time, Hrs.	Pres. Atm.	Deg. Fill.	Al_2O_3 : SiO_2	Products
K 122	200	24	16	.36	10 : 0	Boehmite
K 53	200	24	16	.31	1 : 2	Bayerite, amorphous silica
K 120	250	24	41	.36	10 : 0	Boehmite
K 99	250	24	41	.36	2 : 1	Boehmite, (kaolinite ?)
K 93	250	24	41	.36	1 : 1	Kaolinite, boehmite
K 87	250	24	41	.36	1 : 2	Kaolinite
K 103	250	24	41	.36	1 : 10	Kaolinite, amorphous silica
K 119	300	7	87	.36	10 : 0	Boehmite
K 44	300	7	87	.36	6 : 1	Boehmite, (kaolinite)
K 97	300	7	87	.36	2 : 1	Boehmite, (kaolinite ?)
K 36	300	24	87	.36	1 : 1	Kaolinite, boehmite
K 30	300	24	87	.36	1 : 2	Kaolinite
K 62	300	24	87	.31	1 : 2	Kaolinite
K 79	300	7	87	.36	1 : 2	Kaolinite
K 15	300	120	87	.16	1 : 2	Kaolinite
K 16	300	24	87	.16	1 : 2	Kaolinite
K 17	300	2	87	.16	1 : 2	Kaolinite
K 88	300	7	80	.04	1 : 2	Kaolinite
K 69	300	24	87	.31	1 : 6	Kaolinite, amorphous silica
K 24	300	24	87	.16	1 : 6	Kaolinite, amorphous silica
K 95	300	7	87	.36	1 : 10	Kaolinite, amorphous silica
K 18	350	24	168	.16	1 : 2	Kaolinite
K 19	350	24	168	.34	1 : 2	Kaolinite
K 153	350	24	90	.036	1 : 2	Kaolinite
K 107	350	8	22	.008	1 : 2	?
K 121	400	7	304	.40	10 : 0	Boehmite
K 42	400	7	304	.40	6 : 1	Boehmite, (kaolinite)
K 98	400	7	300	.36	2 : 1	Boehmite, (kaolinite?)
K 100	400	7	300	.36	2 : 1	Boehmite, (kaolinite?)
K 37	400	24	304	.40	1 : 1	Kaolinite, boehmite
K 38	400	7	300	.36	1 : 1	Kaolinite, boehmite
K 27	400	20	300	.36	1 : 2	Pyrophyllite, (kaolinite), (boehmite?)
K 20	400	5	300	.36	1 : 2	Pyrophyllite, (kaolinite), (boehmite?)
K 90	390	7	298?	.36	1 : 2	?
K 91	400	7	300	.36	1 : 2	?
K 92	400	7	225	.11	1 : 2	Pyrophyllite, (kaolinite), (boehmite?)
K 102	400	7	300	.36	1 : 4	Pyrophyllite
K 134	400	7	300	.36	1 : 4	Pyrophyllite
K 41	400	7	300	.36	1 : 6	Pyrophyllite, amorphous silica
K 96	400	7	300	.36	1 : 10	Pyrophyllite, amorphous silica
K 125	400	7	300	.36	0 : 10	Amorphous
K 124	500	7	540	.40	10 : 0	Corundum
K 110	500	7	540	.40	6 : 1	Al silicate, boehmite
K 150	500	7	540	.40	6 : 1	Al silicate, boehmite
K 109	500	2	540	.40	2 : 1	?, Al silicate
K 25	500	24	528	.36	1 : 1	?
K 108	500	3.5	540	.40	1 : 1	?
K 21	500	22	528	.36	1 : 2	Pyrophyllite, (+ ?, like *K* 108)
K 106	500	3	429	.20	1 : 4	Pyrophyllite
K 159	500	7	225	.08	1 : 4	Pyrophyllite
K 40	500	7	540	.40	1 : 6	Pyrophyllite, amorphous silica
K 155	500	7	540	.40	0 : 10	Amorphous

Identification and descriptions of the minerals produced:

1. **Kaolinite**—See (135).

2. **Boehmite,** $Al_2O_3 \cdot H_2O$—X-ray diagram matches that of the natural mineral closely. No diagram is given but there is a table of positions and intensities of the lines. $n = 1.637$ against 1.64 for the natural mineral.

3. **Bayerite,** $Al_2O_3 \cdot 3H_2O$—Unknown in nature. Diagram agrees with Fricke's diagrams from bayerite. A table giving the positions and intensities of the lines is given. $n = 1.572$. The water content corresponds to the formula given above.

4. **Pyrophyllite**—X-ray diagram corresponds in general with one from natural mineral, but many of the lines are out of position by two to four times the error allowable in measuring. No actual diagrams are given, but two sketches are included, one from natural pyrophyllite, and one from the synthetic product; a table of the lines is also given. Dehydration data in the literature are not in good agreement, so Noll dehydrated some pure natural material from Boa Vista, Brazil, and then some of the material that he had prepared. The two curves were practically identical above 400° C., but were much farther apart at lower temperatures, the natural material having 4.93% water and the artificial product 5.67% at 110°. It is concluded that if this product is not true pyrophyllite it at least belongs to the same group of minerals. Mean index is 1.588.

5. **Corundum**—Hexagonal plates parallel to (0001). Mean index is about 1.76.

6. Needles of an **aluminum silicate,** anhydrous, parallel extinction, positive elongation. $\gamma = 1.634$; $\alpha = 1.620$. Sheaf-like forms are present but not common. Occurs in alumina rich mixtures such as $6Al_2O_3 : SiO_2$. Like Schlaepfer and Niggli's No. 9 (85).

7. **Montmorillonite**—Comparison of the X-ray diagram with that of the natural mineral is "satisfactory." Diagrams from natural and synthetic material are reproduced and a table of the lines is given. $n = 1.498 \pm .008$. Slight changes in the spacing of the lines were observed with changing water content, but this is characteristic of the natural mineral.

Discussion of results; conclusions: Noll sought to determine whether the formation of kaolin has a definite "kindling temperature." He obtained **kaolin** in 24 hours at 217° with a mixture of *boehmite, bayerite,* and silica. *Bayerite* and silica gave **kaolin** in 7 hours at 240°, but none in 7 hours at 235°, or in 24 hours at 230°. However, *bayerite* and silica gave **kaolin** in 108 hours at 235° and in 111 hours at 220°. The conclusion from these experiments is that the temperature of formation depends upon the time and the

components; therefore, kaolin may be formed in nature at lower temperatures than those at which it has been produced in the laboratory.

To determine the influence of the character of the solutions mixtures of identical composition were tried with solutions of different pH values, under conditions that were otherwise identical. A mixture of *bayerite*, *hydrargillite*, and amorphous silica, in which the ratio of alumina to silica was one to four, was heated to 300° in a bomb with the degree of filling .36, which developed a pressure of 87 atmospheres, for 20 hours, with different solutions, as follows: N/100 HCl, pure water, N/1000 NaOH, and N/100 NaOH all produced **kaolinite,** but N/10 NaOH produced **montmorillonite.** The last experiment was repeated four times, with the formation of **montmorillonite** each time.

The results are discussed at considerable length and comparisons are made by means of supplementary tables of certain results selected from the main table. The formation of these minerals in nature is also discussed at length and various occurrences of each are cited in correlating the experimental data with field evidence. The following are the principal conclusions concerning the experimental work:

(1) Mixtures with $Al_2O_3 : SiO_2 = 1 : 2$ when heated at 250–300° yield **kaolinite.** Mixtures richer in silica have in addition amorphous silica: those richer in alumina, **boehmite.**

(2) At 400–500° mixtures with $Al_2O_3 : SiO_2 = 1 : 2$, or richer in silica, produce **pyrophyllite.** At 500° 1 : 4 mixtures produce **pyrophyllite;** those richer in silica have amorphous silica remaining. At 500° 1 : 2 mixtures have in addition to **pyrophillite** an **unknown crystalline phase** (indicated in the table by a question mark), which is the only crystalline phase present in a 1 : 1 mixture above 500°.

(3) A **sillimanite-like mineral** appears in mixtures where $Al_2O_3 : SiO_2 = 2 : 1$, at 500°, and becomes most abundant in mixtures where the ratio is 6 : 1.

(4) *Bayerite*, when heated alone, goes over to **boehmite** below 400°, but when it is mixed with a little silica it remains bayerite above that temperature.

(5) Pure alumina gives **corundum** first at about 500°, but with a little silica **boehmite** and **aluminum silicate** are formed.

(6) Amorphous silica remains amorphous at 500°.

1935 **142** NOLL, W.: Hydrothermalsynthetische Untersuchungen im System Al_2O_3-SiO_2-H_2O, *Fort. Min. Krist. Pet.*, **19**, 46–7.

A brief summary of the work recorded in (141). Remarks that the appearance of **pyrophyllite** at high temperatures in the labora-

1935 **143**

1935 **144**

1935 **145**

tory is in accord with its natural occurrences, which are in part pegmatitic. **Halloysite** is stable only at low temperatures. **Montmorillonite** is also stable under hydrothermal conditions, which agrees with its occurrences in nature.

U. Hoffman adds a comment that the layers of aluminum hydroxide and " silicon hydroxide " in halloysite are superposed very much as in kaolinite. He assigns to it the formula $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$. He found *halloysite* to give up part of its water by heating to 50°, or by drying over a desiccant, and at first thought the product to be kaolinite, but later experiments showed the X-ray pattern to be different from that of kaolinite.

Correns and Mehmel heated *halloysite* to 105° and thought that it remained unchanged, but other experiments confirmed a transformation above 50° to **metahalloysite,** which is clearly different from kaolin optically as well as according to X-ray diagrams.

No X-ray or optical data are given in the paper.

1935 **143** NOLL, W.: Synthese des Montmorillonites, *Naturwiss.*, **23**, 197.

Mixtures of *boehmite* or *bayerite* and amorphous silica with $Al_2O_3 : SiO_2 = 1 : 4$ when treated with 0.1 N NaOH solution at 300° C. and 87 atmospheres, gave a material whose X-ray pattern was practically identical with that of **montmorillonite** and whose optical properties and dehydration curve checked fairly well with those of natural montmorillonite. None of these properties are given in this short paper. See (141) and (152) for details.

1935 **144** SCHWARZ, R., AND TRAGESER, G.: Künstliche Umwandlung von Feldspäten in Pyrophyllit, *Naturwiss.*, **23**, 512.

A continuation of earlier experiments on the feldspars (133), but at higher temperatures than those at which **kaolinite** was produced. **Pyrophyllite** was obtained by treating *orthoclase* or *anorthite* in pressure bombs with N/2 HCl at temperatures above 400° C. The product was identified by means of X-ray diagrams and dehydration curves, which are not reproduced in the paper. The kaolin-pyrophyllite point, at about 400°, is suggested as a possible one in geologic thermometry. See (145) for details.

1935 **145** SCHWARZ, R., AND TRAGESER, G.: Über die Synthese des Pyrophyllits, *Zeit. anorg. Chem.*, **225**, 142–50.

The belief is reiterated that *feldspar* breaks up into colloidal alumina and silica and that these products recombine to form the hydrous aluminum silicates, the ones formed being determined by temperature, pressure, and pH value. 1.5 g. samples of *potassium feldspar,* and 2.0 g. samples of *plagioclase* and *kaolin* were treated with 80 cc. of N/2 HCl in a bomb of 160 cc. capacity at temperatures ranging from 180–540° C. In each run 40 cc. of water were

placed in the bomb, but outside of the large crucible that held the mineral and HCl.

The products were identified by means of their dehydration curves and X-ray diagrams. Kaolinite and boehmite lose most of their water at a little over 400° while pyrophyllite and montmorillonite require something over 600°. Therefore, the ratio of the height of the step on a given dehydration curve at 400° to the height of the one at 600° is taken as a rough measurement of the amount of **kaolinite** and/or **boehmite** to the amount of **pyrophyllite** and/or **montmorillonite** produced in the experiment. The dehydration curves for all of the experiments and two for natural pyrophyllite are reproduced in the paper, but no optical data are given, and no X-ray data beyond the generalities mentioned above.

The following table gives the results of the experiments:

Original Mineral	Temp. °C.	Time, Hrs.	Products
K-feldspar	180	60	Bases dissolved from feldspar
"	320	115	Kaolinite
"	400	60	Kaolinite, pyrophyllite
"	450	24	Kaolinite (?), pyrophyllite
"	500	60	Pyrophyllite, boehmite (?)
"	530	90	Pyrophyllite, boehmite (?)
Plagioclase	200	75	Bases dissolved
"	320	60	Kaolinite
"	470	70	Kaolinite (?), pyrophyllite
"	540	90	Pyrophyllite, boehmite (?)
Kaolin	450	40	Remained kaolin
Kaolin[1]	450	60	Kaolin (?), pyrophyllite
Kaolin[1]	532	55	Pyrophyllite, boehmite (?)

[1] SiO_2 added so that the ratio $Al_2O_3 : SiO_2 = 1 : 4.4$.

The amount of **pyrophyllite** increases with increasing temperature to a maximum at about 470°, after which it decreases. This decrease is ascribed to volatility of silica at higher temperatures, which leaves an excess of alumina that hydrates to **boehmite.**

The following course of events is outlined:

(1) Decomposition of the silicates below 200°.

(2) Formation of **kaolinite** from 200° to 400°.

(3) Formation of **pyrophyllite** and **boehmite** from 400° to 550°, with a maximum formation of **pyrophyllite** at 470°.

(4) Above 600° **corundum** forms, indicating that much SiO_2 has been volatilized. No new formation of silicates would be expected above this temperature, with other conditions as in these experiments.

1935 **146** SYROMYATNIKOV, F. V.: The problem of the transfer of silica by water vapors, *Econ. Geol.*, **30**, 89–92.

In an autoclave with an inner volume of 2 liters, $Mg(OH)_2$ was placed in a crucible whose upper rim was 0.8 of the height of the autoclave above its bottom. Freshly precipitated and washed silica gel and water were placed in the bottom of the autoclave. The amount of water taken for each run was sufficiently below the critical volume, about 800 cc. for the 2 liter autoclave, to assure that the upper crucible would not be flooded with liquid water during heating. The following results were obtained:

Exp. No.	H_2O cc.	Temp. °C.	Pres. kg./cm.²	SiO_2 Found in Upper Crucible; % by Weight	Fe_2O_3 Found in Upper Crucible; % by Weight
62	500	400	260	6.00[1]	Not determined
70	400(?)	400	260	4.22	Not determined
128	200	400	220	1.62 to 3.10[2]	Not determined
132	50	350	88	0.20 to 3.10[2]	0.36

[1] The $Mg(OH)_2$ used contained 0.016% SiO_2, the amounts used were not stated.
[2] The SiO_2 was distributed irregularly through the charges, with more near the top.

In another experiment 800 cc. of water and 30 g. of diatomite were heated in the autoclave to 400° C. and a sample of the gas was tapped off at that temperature, condensed and analyzed. It was a turbid, brownish liquid which showed the following content of solids, the volume of liquid analyzed being 260 cc.:

Dry residue on ignition	.4607 g.
Amount of SiO_2 in the residue	.1944
Amount of Fe_2O_3 in the residue	.2368

The material may have been in true solution, or may have been dispersed as a sol, but a more mechanical transfer is impossible. (The possibility of convection currents in the large autoclave is not discussed.)

Serpentine was formed in the upper crucible, which indicates the possibility of the formation of serpentine in nature by pneumatolysis. Attention is called to the fact that the amount of silica carried into the upper crucible in Experiment 62 is more than could be carried in solution in 2 liters of water at 400°, indicating diffusion of silica molecules through the gaseous medium. By a similar process great quantities of silica might be formed in rocks that can react with siliceous vapors, with little or no shifting of the gaseous medium. No properties of the serpentine are given.

1935 **147** VAN NIEUWENBURG, C. J., AND VAN ZON, P. M.: Semi-quantitative measurements of the solubility of quartz in super-critical steam, *Rec. trav. chim.*, **54**, 129–32.

Used a double autoclave to do away with temperature gradient and placed a small platinum crucible containing 100 mg. of quartz on a tripod near the top of the inner vessel. No upper crucible with ZnO was used this time, the solubility being taken as the loss of weight of the crucible, after a correction of − 3.5 mg. had been applied to each determination to allow for combined hydrothermal solution and washing away of entire particles by liquid water.

Three isothermal P-X diagrams are given, at 380°, 400°, and 425° C. The curves are fairly regular and indicate that the solubility of silica increases with increasing pressure at constant temperature and decreases with increasing temperature at constant pressure. The curves are remarkably similar to those predicted by Smits (113). Pressures used were from 295 to 500 kg./cm.², except at 425°, where they were 365 to 500 kg./cm.².

Solubility at 380° = .23 to .49 mg. SiO_2 per cc. steam.
Solubility at 400° = .06 to .45 mg. SiO_2 per cc. steam.
Solubility at 425° = .08 to .40 mg. SiO_2 per cc. steam.

1935 **148** KÖHLER, W.: Über die Bildung kristallisierter Kalziumsilikathydrate, *Tonind.-Zeit.*, **59**, 739–40; 754–6.

Prepared mixtures of composition $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $CaO \cdot SiO_2$, by mixing CaO and amorphous silica in the proper proportions, heating to 1400° C., crushing and heating again, until no further test for free CaO was obtained.

Samples of these mixtures were heated in 50 cc. bombs with sufficient water so that there was always a liquid phase present. Up to 220° the bombs were fastened to a rotating apparatus in an oil bath; above that temperature they were placed upright in a sand bath. After a given run the product was drawn off in such a manner as to exclude CO_2, washed with water-free methyl alcohol, and dried in a desiccator. It was then studied chemically, microscopically, and with X-rays.

1. Tri- and dicalcium silicate mixtures at 150° C. and 5 atmospheres for 3 days gave amorphous products.

2. At 200° C. and 15 atmospheres for 3 days these mixtures gave minute needles, and consisted entirely of the needles after 6 days at 220°.

3. 2 g. of the metasilicate mixture with 8 cc. of water was unchanged up to 290°.

4. 3 g. of the dicalcium silicate mixture with 8–10 cc. H_2O in 10–14 days at 212°, or in 8 days at 290°, changed completely to birefringent material; analysis showed $2.2CaO \cdot SiO_2 \cdot H_2O$. These properties correspond very well with those of **hillebrandite,** $Ca_2SiO_4 \cdot H_2O$, as do the X-ray diagrams (See below).

5. Tricalcium silicate mixture treated in 0.5 to 3 g. samples with 10–40 cc. H_2O for 14–28 days at 212°, or 8 days at 290°, produced the same needles, and in addition, strongly birefringent crystals of **Ca(OH)$_2$**.

Schematic line diagrams prepared from the X-ray photographs of the products of (4) and (5) are reproduced, and for comparison a similar diagram for hillebrandite is prepared from Vigfusson's [1] data. A table of the spacing and intensities of the lines is also given for these two preparations; Vigfusson's data are included in the table for comparison.

The *hillebrandite* loses its water from 300° C. to dull red heat. It retains its crystal form, but X-ray diagrams show that it has reverted to the anhydrous **calcium orthosilicate,** $2CaO \cdot SiO_2$. X-ray line diagrams and tables, like those described above for hillebrandite, are given for this dehydrated product, and for comparison, Vigfusson's data for calcium orthosilicate are given. The product from the tricalcium silicate gives, on dehydration, CaO in addition to the orthosilicate.

Nagai's (122) preparation of afwillite could not be duplicated, but **xonotlite** was prepared in the bomb from CaO and SiO_2, the latter either as *quartz* or amorphous silica. In some of these runs **hillebrandite** was formed and in still others **Ca(OH)$_2$** and an **unidentified crystalline phase** also appeared. The unidentified crystals have an index of 1.60, which is too low for afwillite.

1936 **149** CHITAROW, N. I., AND IWANOW, L. A.: Kritische Temperatur des Wassers und der wässerigen Lösung des kieselsauren Natriums, Zentr. Min., **1936**, 46–54.

Re-determined the critical temperature of water, using a tube like the one devised by Nadeschdin (*Nachrichten der Universität in Kiew*, Nr. 6, 1885); checked some of Schroer's (*Zeit. phys. Chem.*, vol. 129, pp. 79–110, 1927) work with KCl, and determined the critical temperature of solutions of sodium silicates. Critical temperature of water is 374° C.; 0.5 N Na_2SiO_3, 391.9°; 1.0 N Na_2SiO_3, 400.8°; 1.2 N Na_2SiO_3, 402.1°.

The same apparatus was used to demonstrate that these solutions lose none of their dissolved material on passing into the supercritical state.

1936 **150** GRUNER, J. W.: Hydrothermal alteration of montmorillonite to feldspar, *Am. Mineral.*, **21**, 201. (Abstract.)

Montmorillonite was heated in gold-lined pressure bombs in

[1] Am. J. Sci., (5), 21, 1931, p. 67. Presumably drawn from the data in Vigfusson's table of lines for hillebrandite, since he does not give any actual photographs or line diagrams in his paper.

aqueous solutions of $KHCO_3$ (10%). Seven days at 300° C. produced very good **orthoclase.** The X-ray powder photograph is identical with that of **adularia.** At 272° C. the feldspar pattern became distinct after 10 days. At 245° C. the stronger lines of orthoclase appeared after 42 days heating. No changes were noticeable after four weeks at 200° C. KCl solutions do not seem to alter the *montmorillonite* in 19 days at 300° C. See (151) for details.

1936 151 GRUNER, J. W.: Hydrothermal alteration of montmorillonite to feldspar at temperatures from 245° C. to 300° C., *Am. Mineral.*, **21**, 511–515.

Used *montmorillonite* from an unknown locality which, however, gave a typical and unmistakable X-ray diagram. For a given run a half gram sample was put into a 50 cc. gold-lined bomb with 10 cc. of a solution of 1 g. of $KHCO_3$ in 10 cc. of recently distilled water. The air in the bomb was displaced by CO_2. The bomb was then heated to the desired temperature and held there for a given time. The products were so fine grained that no optical tests could be applied, except a rough determination of the index, which lay in the **orthoclase** range. X-ray patterns were relied upon chiefly for identification. No diagrams are reproduced, but a table is included, giving the positions and intensities of the lines of diagrams from typical adularia, and the synthetic feldspar prepared at 245°, 272°, and 300°.

Muscovite, which by reason of its structural similarity might have been expected to form, was not found in any of the preparations.

The results recorded are exactly those given in the abstract (150) and need not be repeated.

1936 152 NOLL, W.: Synthese von Montmorilloniten, *Chemie der Erde*, **10**, 129–54.

Mixtures of precipitated alumina, which consisted largely of a mixture of *bayerite* and *hydrargillite*, and amorphous silica were treated in a 6 cc. bomb with 2 cc. portions of solutions of NaOH, KOH, CsOH, $Ca(OH)_2$, $Mg(OH)_2$, and $Be(OH)_2$ of various concentrations; also with one concentration each of HCl, NaCl, Na_2SO_4, $MgSO_4$, and KCl. Samples were also treated with pure water. The mixtures had a ratio of $Al_2O_3 : SiO_2 = 1 : 4$. The bomb was heated at the rate of 100° in 20 to 30 minutes to 300° C., where it was held for 15 to 24 hours and cooled at approximately the heating rate. Pressure was 87 atmospheres. Degree of filling for all runs was .35. Amounts of material used in the runs are indicated in the following table, as are the results:

Solution	Time	Mg. Al_2O_3	Mg SiO_2	Mg. R'OH or $R''(OH)_2$	Ratio Alk/Al/SiO_2	Product as Shown by X-rays
n/100 HCl	18	50	117.8	—	—	Kaolinite
H_2O	15	50	117.8	—	—	Kaolinite
"	20	25	58.9	—	—	Kaolinite
NaOH	16	50	117.8	0.062	.002 : 1 : 4	Kaolinite (+ Montmorillonite?)
"	16	50	117.8	0.62	.02 : 1 : 4	Kaolinite and Montmorillonite
"	20	100	235.6	6.2	.1 : 1 : 4	Montmorillonite and Kaolinite
"	24	50	117.8	4.65	.15 : 1 : 4	Montmorillonite (+ Kaolinite)
"	20	50	117.8	6.2	.2 : 1 : 4	Analcite
"	20	50	117.8	31.0	1 : 1 : 4	Kaolinite
KOH	20	50	117.8	1.1	.02 : 1 : 4	Montmorillonite (+ Kaolinite)
"	20	50	117.8	11.0	.2 : 1 : 4	Amorphous
"	20	50	117.8	55.0	1 : 1 : 4	Montmorillonite (?)
CsOH	24	50	117.8	29.39	.2 : 1 : 4	Kaolinite
$Ca(OH)_2$	20	50	117.8	.73	.02 : 1 : 4	Montmorillonite
"	20	50	117.8	7.3	.2 : 1 : 4	?
"	20	50	117.8	36.5	1 : 1 : 4	Kaolinite
$Mg(OH)_2$	20	50	117.8	.57	.02 : 1 : 4	Montmorillonite
"	20	50	117.8	5.72	.2 : 1 : 4	Montmorillonite
"	20	50	117.8	17.96	.63 : 1 : 4	Montmorillonite
"	20	50	117.8	28.50	1 : 1 : 4	Montmorillonite
"	20	50	117.8	57.15	2 : 1 : 4	Montmorillonite
$Be(OH)_2$	20	50	117.8	4.22	.2 : 1 : 4	Montmorillonite (+ Kaolinite)
"	20	50	117.8	42.2	2 : 1 : 4	Montmorillonite (+ Kaolinite)
NaCl	24	50	117.8	11.5[1]	.2 : 1 : 4	Kaolinite (+ Montmorillonite)
Na_2CO_3	24	50	117.8	8.2[1]	.2 : 1 : 4	Montmorillonite (+ Kaolinite)
$MgSO_4$	24	50	117.8	4.0[1]	.2 : 1 : 4	Montmorillonite (+ Kaolinite)
KCl	24	50	117.8	14.6[1]	.2 : 1 : 4	Kaolinite (+ Montmorillonite)

[1] Milligrams of the salt, not the oxide equivalent.

The products were too fine grained for optical determination (.5μ to 200Å) and the identifications were by means of X-ray photographs. Three of these are reproduced for one of the **montmorillonite** preparations, in different stages of hydration. A table is included in which are given the positions and intensities of the lines from eight of the preparations, and from natural montmorillonite and kaolinite.

In general **kaolinite** was formed with HCl, H_2O, and in alkaline solutions up to about .02 : 1 : 4 (alkali : alumina : silica). With increasing basicity **montmorillonite** is formed up to 1 : 1 : 4 with NaOH, KOH, and $Ca(OH)_2$, beyond which a new phase is formed, which is **analcite** with NaOH. Both **kaolinite** and **montmorillonite** were formed when solutions of salts were used in the ratio .2 : 1 : 4.

These results indicate that in nature kaolin may be formed where the solutions are acidic, neutral, or slightly alkaline; montmorillonite, where the solutions are slightly more alkaline; and the zeolites, where the solutions are still more alkaline.

1936 STRAUB, F. G.: Analcite: Preparation and solubility between
153 182° and 282° C., *Ind. Eng. Chem.*, **28**, 113–14.

Analcite was prepared in a bomb from sodium silicate, sodium aluminate, and water, by heating to 282° C. for 46 hours. In the first series of experiments 70 cc. of a solution of sodium silicate containing 10.8 g. of silica, and 8 g. of solid sodium aluminate containing 4.6 g. of alumina, were placed in a bomb with 40, 110, and 260 cc. of water, in successive runs. The volume of the bomb is not given. The run with 260 cc. of water produced the largest crystals of **analcite,** which averaged about 0.1 mm. in diameter. The product in every case was practically identical with that of natural analcite. In a later experiment 80 cc. of the sodium silicate solution were used with 10 g. of the solid sodium aluminate and 302 cc. of water. The composition of the resulting crystals was the same, but they averaged only .02 mm. in diameter.

"Solubility" tests were performed with water and with NaOH of various concentrations up to 3.5 millimoles per liter. For these tests a bomb was used that was fitted with an upper compartment and an intermediate valve for drawing off some of the solution after equilibrium was reached. For a description of this apparatus see *Ind. Eng. Chem.*, **24**, p. 914, 1932. The quantitative results are given in the following table; they have no necessary connection with the "solubility" of analcite.

Test	Temp. °C.	Added NaOH	Found in Solution				Ratio SiO_2/Al_2O_3
			NaOH	Na_2CO_3	Al_2O_3	SiO_2	
			Millimoles per liter				
612 –1	182	0	1.64	0.41	0.32	0.72	2.20
2		0	2.47	0.65	0.34	0.90	2.62
3		2.4	1.28	1.61	0.27	1.21	4.45
4		2.4	1.02	1.30	0.28	0.93	3.26
5		5.9	3.00	3.36	0.43	1.65	3.79
6		5.9	3.26	3.47	0.42	1.85	4.38
613– 7	207	0	0.44	0.85	0.57	1.41	2.44
8		0	0.50	0.96	0.45	1.28	2.79
9		2.5	0.71	1.25	0.45	0.80	1.77
10		2.5	1.02	1.55	0.52	1.06	2.01
12		6.2	2.80	3.48	0.45	1.87	4.16
13		6.2	3.24	3.56	0.52	1.66	3.16
614–13	243	0	0.31	0.98	0.57	1.51	2.64
14		0	0.58	1.03	0.53	1.75	3.26
15		0.25 (?)	0.97	2.28	0.46	1.82	3.95
18		2.50	0.93	2.24	0.48	1.73	3.56
19		6.20	2.90	3.95	0.88	2.46	2.78
20		6.20	3.57	3.92	0.84	2.10	2.50
615–21	282	0	0.46	1.38	0.78	2.20	2.79
22		0	0.25	1.06	0.62	1.80	2.86
23		2.50	0.75	2.55	0.70	2.32	2.30
24		2.50	0.89	2.24	0.64	2.20	3.43
25		6.25	3.38	4.01	0.96	2.82	2.93
26		6.25	3.33	4.06	1.03	2.50	2.43

1936 **154** FORET, JEANNE: Synthèse sous pression de silicates monocalciques hydratés, *Compt. rend.*, **203**, 80–3.

Autoclaved mixtures of CaO and *quartz* with a molecular ratio of $Ca \cdot OSiO_2$ at temperatures from 100–200° C., under a pressure of ca. 100 kg./cm.² of nitrogen. Two structurally different forms of **monocalcium silicate hydrate** were obtained, the form that appears in cement being stable up to 140° and a different crystalline form above that temperature. The products were studied chemically, microscopically and by means of X-rays, but no data or properties are given except the amounts of water in the hydrates prepared at different temperatures and a table giving the positions and intensities of the principal X-ray lines of each form. The degree of hydration depends upon the temperature and is independent of the pressure (from 20 to 168 kg./cm.²). It is less at higher temperatures, the hydrate prepared at 130° being $CaO \cdot SiO_2 \cdot 8H_2O$, and that at 190° being $CaO \cdot SiO_2 \cdot 0.25H_2O$ (**xonotlite**?).

Rate of reaction was studied by estimating by chemical and microscopical means the amount of quartz left after 22 hours at

various temperatures and pressures. The rate increases rapidly with increasing temperature but is not appreciably affected by pressure.

1936 155 NOLL, W.: Ueber die Bildungsbedingungen von Kaolin, Montmorillonit, Sericit, Pyrophyllit, und Analcim, *Min. petr. Mitt.*, **48**, 210–47.

A summary and correlation of the previously published results concerning syntheses of these minerals, (124), (125), (135), (141), (143), and (152). Also a discussion of their natural occurrences and a comparison of the conditions of formation deduced from such occurrences with those found in laboratory experiments. For the experimental methods, identification of the products, and detailed results, see the abstracts of the earlier articles.

The following general conclusions concerning the conditions of formation of these minerals in hydrothermal syntheses are given:

1. **Kaolinite** forms by the reaction of alumina and silica in neutral alkali-free solutions, or in acidic alkali-containing solutions, below 400° C. Excess alumina crystallizes to **boehmite;** excess silica remains amorphous. See (141) for details.

2. **Montmorillonite** forms from mixtures that have a moderate amount of alkali or alkaline-earth metal present, when the solution is alkaline. The best concentrations of K, Na, Ca, and Mg for its formation are somewhat different, having a considerably greater range for magnesium than for any of the others. See (152) for details.

3. **Sericite** forms from mixtures in which the amount of K_2O present is approximately the ideal amount indicated by the muscovite formula, when the solution is alkaline, hence from mixtures richer in alkali than those producing montmorillonite. See (123) and (124) for experimental results.

4. **Zeolites** form from mixtures still richer in alkalis and more strongly alkaline. **Analcite** forms in the system with soda when the amount of Na_2O present is too high for the formation of montmorillonite.

5. **Pyrophyllite** forms from mixtures like those that produce kaolinite, and with the same kinds of solutions, but is formed above 400° C. instead of below.

6. Halloysite is not stable above 50° C., hence it does not appear in any of the hydrothermal experiments. It does not form at lower temperatures in the laboratory because the reaction that produces it is too slow.

These observations indicate that the boundaries of the regions of stability for kaolinite, montmorillonite, sericite and zeolites

(below 400° C.), are determined by the alkali concentration of the mixture and the pH value of the solution. The boundary between the regions of stability of kaolinite and pyrophyllite seems to be one of temperature alone. This boundary occurs at approximately 400° C., a point that may be useful as a point in geologic thermometry.

The natural occurrences of these minerals are discussed at considerable length and the following conclusions are drawn concerning their formation in nature:

1. Kaolin forms from alkali feldspars when much of the alkali is carried away, or when the active solutions are acidic. The former condition commonly prevails in strong chemical weathering.

2. Pyrophyllite forms under the same chemical conditions, except at higher temperatures.

3. Sericite is formed when less alkali is carried away.

4. Montmorillonite forms with a lower total alkali content than that prevailing when sericite is formed, but with the solutions still alkaline.

5. Zeolites form where there has been very slight transport of alkalis and the solutions are comparatively strongly alkaline.

6. The rate of transport of alkali away from the mineral or rock being altered and the rate of reaction are important in determining what the product or products will be when a given solution alters a given mineral or rock. For example, in the alteration of orthoclase near the top of the kaolin temperature range, silica and alumina may react readily and incorporate the K_2O in sericite before it has time to get away, whereas the same solution might give rise to kaolin from orthoclase at lower temperatures, because the reaction would be so slow that the K_2O could be carried away before reaction took place. Also, bentonite commonly forms from glassy rocks because in the glassy state the reaction takes place readily even at low temperatures and incorporates the alkali and alkaline-earth metals before they are taken away.

The natural occurrences seem to fit into the general picture obtained from the syntheses.

1937 NORTON, F. H.: Accelerated weathering of feldspars, *Am. Min.*,
156 **22**, 1–14.

A study of the alteration of *orthoclase*, *anorthite*, and *albite* by H_2O and CO_2 below 350° C. The innovation in technique is the constant percolation of fresh liquid through the powdered mineral, with consequent removal of the soluble products of reaction. This technique may explain the formation of sericite and pyrophyllite at temperatures considerably below those at which they have usually

been reported. The feldspar is ground to a very fine powder (< 1 micron) and a sample placed in a thin alumina cup that is held above the water level of the reaction chamber on a wire support. The fresh liquid is supplied by condensing it on a U-shaped tube that is silver-soldered through the top of the reaction chamber. Air is drawn through the tube at such a rate that the liquid condenses on it and drops onto the powdered mineral just as fast as it can percolate through the sample and the porous alumina cup.

For each run the reaction chamber is filled about one-third full of water and, after the mineral sample is in position, solid CO_2 is placed in the chamber. By bolting the top down only partially at first and then tightening it when the CO_2 has all vaporized and the pressure has come to the desired value, the CO_2 pressure (cold) can be controlled accurately. No solvent other than CO_2-charged water was tried.

The following results are recorded:

Run	Mineral	T.°C.	CO_2 Pressure Cold lbs./sq.in.	Total Pressure Hot lbs./sq.in.	Time in Days	Results
2	Orthoclase	225	15	390	11	Very slight alteration
4	"	320	200	2250	10	Slight alteration
6	"	280	265	1800	10	Slight alteration
6a	"	280	265	1800	21	Considerable change
6b	"	280	265	1800	33	Nearly complete change
7	"	320	525	2950	15	Nearly complete change
8	"	350	500	4000	11	Almost no change
9	"	250	500	2000	12	Slight leak
11	Anorthite	300	260	1950	18	No change
12	"	250	300	1230	23	Slight change
14	"	275	300	1650	24	Considerable change
10	Albite	315	200	2100	19	No change
13	"	250	300	1230	23	Slight change
15	"	275	300	1650	24	Slight change

Sericite was produced by the alteration of *orthoclase*, and **quartz** was deposited on the metal of the reaction chamber at the surface of the water.

Pyrophyllite and **calcite** were produced by the alteration of the *anorthite*.

The *albite* was only slightly altered and the product was not identified with certainty. The evidence obtained suggested **paragonite** (?).

These products were identified by means of X-ray and microscopic studies. The **sericite** from *orthoclase* was further studied by means of thermal curves and loss on ignition. X-ray diagrams of unaltered and altered *anorthite* and *albite* are given. Microphotometer curves of the X-ray patterns from the product of each of four runs in which **sericite** was produced from *orthoclase* are given and, for comparison, curves from the diagrams of orthoclase, muscovite, sericite, and kaolinite. Thermal curves for the products of two of these runs are given and, for comparison, thermal curves for muscovite and kaolinite. Tables of the spacing and intensities of the lines in the X-ray diagrams of untreated and treated anorthite and albite, and of pyrophyllite, calcite, sericite, and the unidentified product from albite are given. No optical properties of the products are recorded.

MINERAL INDEX

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Actinolite, alteration of			(94)
Adularia	245°(150)	300° (36,150)	(?36), (150)
Alteration of			(26, after fusion), (31), (75), (88)
Aegirine-augite		420°	(75)
Aegirine, potassium		470°	(84)
Afwillite	100°(110)	200° (110,122)	(?110), (122)
Alamosite	300°(104)	550°(104)	(104), (115)
Albite	380°(116)	520°(71)	(23), (59), (71), (?73), (78), (91), (116)
Alteration of			(26, after fusion), (26), (31), (36a), (40), (88), (103), (156)
Alkali aluminosilicates	100°(26)	210°(41)	(26), (41)
Allophane			(?99)
Alteration of			(26)
Al_2SiO_5	450°(78)	Red heat (16)	(16), (78), (?85), (?141)
Aluminum silicate. Hydrous	470°(85)	Red (16)	(16), (78), (85), (101), (141) (36a)
Alunite		22–200°	(103)
Amianthus		300°	(?101)
Amphibole	375°(74)	470°(85)	(48, Hb), (74, Mg), (76, Trem.), (85, Ca), (127, Hb), (131, Hb)
Analcite	100°(91)	550°(48)	(10), (17), (20), (23), (26), (31), (40), (43), (?48), (?56), (59), (73), (78), (88), (91), (116), (152), (153), (155)
Alteration of			(31), (40, after fusion), (56), (73), (116)
Analcite, basic		185°	(?26)
Analcite, potassium		360–400°	(?79)
Andalusite		450°	(78)
Attempted alteration of			(138)
Andesine, alteration of			(40), (41, after fusion)
Anorthite	470°(85)	500° (45, 47)	(45), (47), (85)
Alteration of			(26), (31), (40), (43), (94), (133), (144), (156)
"Anorthite, sodium"		Fusion	(56)
Alteration of			(56)
Anorthoclase		360°	(75)
Anthracite		400°	(?5)
Antigorite	365°(116)	380°(115)	(115), (116)
Apophyllite	155°(43)	210°(86)	(2), (43), (86)
Alteration of			(26), (58, attempted)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Augite			
Aegirine	470°		(75)
Hedenbergitic	400°(5)	470°(85)	(5), (85)
Alteration of			(26), (77)
Babingtonite	470°		(?85)
$BaO \cdot 2SiO_2$	300–550°		(104)
Solid solution with $2BaO \cdot 3SiO_2$			(?104)
Basalt, alteration of			(26)
Heat in evacuated tubes			(130)
Bauxite, as a reagent			(6)
Bayerite	Room temp.		(141)
As a reagent			(141), (143), (152)
Beidellite	350–390°		(138)
Beryl, de- and rehydration of			(76)
Biotite	500°(47)	Red (53)	(?47), (?53)
Alteration of			(75), (93)
Boehmite	Room (107, 141)	500°(141) 540°?(145)	(?96), (?107), (138), (141), (145), (155)
As a reagent			(138), (141), (143)
Boric acid (H_3BO_3)	Room		(104)
Brucite	400°		(51)
Bytownite, alteration of			(103)
Ca-Al silicate, hydrous	500°		(45)
Calcite	Room (137)	500°(32) 535°?(49)	(26), (32), (49), (75), (78), (85), (?86), (91), (94), (115), (116), (137), (156)
Alteration of			(75)
As a reagent			(?31), (86), (94)
Calcium aluminate	470°		(?85)
Calcium amphibole	470°		(85)
Calcium chlorosilicate	Red		(28), (39)
Calcium hydroxide	100°(110)	290°(148)	(110), (137), (148)
As a reagent			(137)
Calcium orthosilicate	132°(121)	300°(148) Red(28,39)	(28), (39), (?85), (?121), (148)
Hydrous	150°(137)	290°(148)	(122), (137), (148)
Calcium oxychloride	470°(85)	Red (28)	(28), (?85)
Calcium silicate	300°		(101)
Hydrous	153–200°		(122)
Cancrinite	200–220°		(40)
Cancrinite-like mineral	185°(26)	500°(50)	(26), (40), (50)
Cancrinite, sodium $CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot H_2O$	500°(All)	530°(59)	(50), (59), (70) (?140)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
$4CaO \cdot 2Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$	500°(46)		(46), (47)
$6CaO \cdot 3Al_2O_3 \cdot 3SiO_2 \cdot 2CaCl_2$	Red heat		(39)
$3CaO \cdot 2SiO_2$	131–213°		(?121)
$3CaO \cdot 2SiO_2 \cdot H_2O$	180–200°		(?122)
$CaSiO_3$ (See also wollastonite)	132°(121)	Red (28, 39)	(28), (39), (?121)
Hydrous; see also xonotlite	100–200°		(154)
Cd_2SiO_4	365–395°		(116)
Celestite	365°		(115)
Centrallasite	420°		(?91)
Chabazite	150°(43)	200° (40, 43)	(?40), (43)
Alteration of			(31)
Chalcedony	300°(75)	400°(5)	(5), (75)
As a reagent			(22)
Chalcocite		<280°	(88)
Chlorite	400°(93)	600°(82)	(77), (82), (91), (93)
Alteration of			(91, recrystallized)
Clay minerals; see allophane, beidellite, dickite, halloysite, kaolin, montmorillonite, nacrite, and nontronite.			
Clay, alteration of			(39), (140)
Clinoenstatite	365–380°		(115)
Copper	415°(116)	600°(82)	(82), (116)
Corundum	300°(42) with NH_4F	600°(145)	(6), (15), (42), (49), (?73), (85), (141), (145)
Alteration of			(54)
Cristobalite	180°(57)	1200°(130)	(57), (81, changed to quartz), (100), (?104), (130), (138)
Cryolite	350–500°		(103)
Crystalline phases not identified (See "Unidentified crystals")			
Cyanite; see kyanite			
Datolite	400°		(52)
Alteration of			(26), (31)
Dawsonite	185°		(?56)
Devitrite	550°		(104)
Diaspore	90°(73)	450°(49)	(49), (56), (?73)
Alteration of			(54)
Dickite	225°?(119)	365°(138)	(?119), (138)
Diopside	395°(115)	550°(48)	(48), (115)
Alteration of			(75), (77)
Epidote, alteration of			(94)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
"Faujasite, potassium"	450°		(?78)
Fayalite	470°(85)	Red (27)	(27), (85)
Alteration of			(29)
Feldspar, not classified			(5)
Alteration of			(40), (40, after fusion), (108), (132), (133), (145)
Fluorite	20°		(36a)
Alteration of			(75)
Forsterite	375–475°		(74)
Foshagite	170°		(?137)
Garnet	Red heat (25)		(25 Mn), (?25 Gross.), (?39 Gross.), (?FeCa 85), (?131)
Garnierite, alteration of			(92)
Glass			
Glass Used in experiments			(5), (17), (26), (31), (41), (42), (53), (58), (75), (75, obsidian), (89), (104)
Hydration of			(26), (54), (65), (69), (83), (97), (104)
Goethite	470°		(?85)
Granite, alteration of			(36a), (53, after fusion), (75)
Grossularite	Red (25)		(?25), (?39)
Gypsum	Room (110, 137)		(110), (137)
As a reagent			(31)
Gyrolite	420°(91)	450°(78)	(78), (?91)
Halloysite			(?142), (155, reason for non-formation)
Dehydration of			(142)
Haüynite, alteration of			(31), (41)
Hedenbergitic augite	400°(5)	470°(85)	(5), (85)
Hematite	250°(42) NH_4F	500°(49)	(42), (49), (75), (84), (138)
As a reagent			(91)
Heulandite	200°		(43)
"Hieratite"	450°(78)	470°(85)	(78), (85)
Hillebrandite	153°(122)	470°(85)	(85), (122), (?137), (148)
Dedhydration of			(148)
Hornblende	550°(48)		(48), (127), (131)
Alteration of			(76, dehydration), (88)
Hydrargillite	Room (61, 141)		(61), (141)
As a reagent			(141), (152)
Hydrated crystalline silica	180°(8)	320°(101)	(?8), (?101)
Hydrous aluminum silicate			(36a)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Ilmenite	270–300°		(42)
Iron chlorosilicate	Red		(30)
Iron oxide	183°(88)	470°(88)	(56), (85), (88)
Hydrous	420°		(91)
Iron silicate			(101)
Ittnerite, alteration of			(31)
Ittnerite, potassium	200°		(7)
Jadeite, alteration of			(40)
Kaliophilite	200°(106)	600°(82)	(40), (44), (78), (82), (84), (85), (91), (93), (106)
Alteration of			(54), (56), (106), (116)
Kaolinite	20°?(36a, HF)	400°(141)	(?36a), (?84), (?96), (99), (?107),
	225°(119, HF)	470°?	(?108), (?114), (?119), (125),
	250°(125, 135, 141)	(84, 145)	(?128), (132), (133), (134), (135), (138), (141), (144), (145), (152), (155)
Alteration of (mostly kaolin)			(5), (10), (26), (31), (37), (40), (41, after ignition), (54), (56), (106), (107, de- and rehydration), (133), (138), (?140), (145)
K-Ba-Al silicate, hydrous	200°		(7)
K-F-Al silicate	300°		(42)
$KHSi_2O_5$	420–515°		(89)
$(K_2Na_2Ca)O\cdot 3SiO_2\cdot 2H_2O$	180°		(21)
Knebelite	Red		(27)
Alteration of			(29)
$K_2O\cdot Al_2O_3\cdot SiO_2$	Strong red		(37)
$K_2O\cdot Al_2O_3\cdot 2SiO_2$	200°(31)	Red (37)	(31), (37)
K_2SiO_3	610–996°		(89)
$K_2SiO_3\cdot 0\cdot 5H_2O$	370–610°		(89)
$K_2SiO_3\cdot H_2O$	200–370°		(89)
$K_2Si_2O_5$	200–1041°		(89)
$K_2Si_2O_5\cdot H_2O$	280–405°		(89)
Kyanite, attempted alteration			(138)
Labradorite, alteration of			(26, after fusion), (26), (36a), (40), (41, after fusion), (91), (103)
Lead	385°		(115)
Leonhardite, alteration of			(40), (41, after fusion)
Lepidolite, alteration of			(70)
Leucite	100°(31)	500°(44)	(10), (16), (31), (40), (44), (?56), (?79), (91), (116)
Alteration of			(10), (56), (116), (132), (133)
Leverrierite	350–575°		(?103)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Levynite	170°		(7)
LiF	500°		(70)
Li_2SiO_3	500°		(70)
"Lithium nepheline"	200°		(?54)
Magnesite	200°(80)	260°(94) 350°?(80)	(80), (94)
Magnesium amphibole	375–475°		(74)
Magnesium pyroxene	Low red		(14)
Magnesium silicate, basic	220°		(?92)
Magnetite	270° (42, HF)	475°(74)	(42), (74), (85)
"Orthorhombic modification"	470°		(?85)
Manganese chlorosilicate	Red		(30)
Manganese garnet	Cherry red		(25)
Manganese silicate	300°		(?101)
Mesolite	<200°		(?10)
Alteration of			(10)
"Metahalloysite"	>50°		(142)
"Metakaolin"	420–850°		(107)
Rehydration of			(107)
$MgCO_3$	260°(94)	365°(116)	(94), (116)
Basic	60°		(92)
Mica	200?(56) 225°(124)	500°(47)	(?47), (?53), (?56), (78), (?106), (123), (124), (?131)
Alteration of			(44), (45), (46), (47), (50)
Microcline, alteration of			(42), (88), (103)
Montmorillonite	300°(141, 143, 152)		(141), (142), (143), (?145), (152), (155)
Alteration of			(150), (151)
Mordenite	200°		(?103)
Mullite, attempted alteration of			(138)
Muscovite	200°?(56) 225°(124)	450°(78)	(?56), (78), (?106), (123), (124)
Alteration of			(5), (44), (59), (60), (65), (70), (75), (82), (106)
$Na_6Al_6Si_8O_{28}\cdot 5H_2O$	200°		(56)
Nacrite	200°		(?56)
$Na_2O\cdot Al_2O_3\cdot 2SiO_2$	Red		(37)
$4(Na_2O\cdot Al_2O_3\cdot 3SiO_2)\cdot 15H_2O$	200°		(54)
$6Na_2O\cdot 3Al_2O_3\cdot 8SiO_2$	510°		(?67)
$Na_2O\cdot 3CaO\cdot 6SiO_2$	550°		(104)
Na_2SiO_3	500°		(83)
Critical temperatures of solutions of			(149)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
$Na_2Si_2O_5$		300°	(83)
Natrolite	100°(40)	600°(82)	(?10), (?26), (?40), (43), (56), (73), (?77), (82), (106)
Alteration of			(10), (26), (40, after fusion) (41, after fusion), (73)
Natrolite, potassium		200°	(56)
Natrolite, with abnormal water content		200°	(56)
Nepheline	200°(59)	520°(71)	(44), (46), (59), (67), (70), (71), (73), (91), (93), (106)
Alteration of			(10), (26, after fusion), (31), (41, after fusion), (43), (56), (73), (106), (116)
Nepheline, hydrated		200°(54)	(54), (?56)
Alteration of			(54), (56)
Nepheline, lithium		200°	(?54)
Nepheline, potassium (See kaliophilite)			
Nesquehonite		90°	(94)
Nickel silicate		260°	(?94)
Nontronite		350°	(138)
Nosean		500°	(50)
Alteration of			(31)
Nosean, hydrous	100°(26)	500°(47)	(?26), (?47)
Nosean, potassium		200°	(7)
Obsidian			
Alteration of			(36a)
Dehydration of			(97)
Heated in evacuated tubes			(130)
Okenite	200°(43)	470°(85)	(43), (?85)
Alteration of			(26), (43)
Oligoclase		450°	(78)
Alteration of			(36a), (41, after fusion)
Olivine	375°(74)	470°(85) Red (27)	(27, Fa), (74, Fo), (85, Fa), (85, CaFe)
Alteration of			(92), (94), (109)
Opal	Room (4)	470°(85)	(4), (?8), (64), (75), (78), (?85)
Crystallization of			(64)
Orthoclase (See also adularia and potassium feldspar)	360°(79, 91)	550°(48)	(12), (13), (16), (18), (19), (23), (?36), (44), (?48), (53), (71), (73), (78), (79), (84), (85), (91), (116), (150), (151)
Alteration of			(26, after fusion), (26), (36a), (88), (138, attempted), (144), (145), (156)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Palagonite, hydration of			(26)
Paragonite	250–275°		(?156)
Alteration of			(106)
Pectolite	195°(31)	450°(78)	(5), (26), (31), (78), (91)
Penninite	560°		(?77)
Periclase	Low red		(15)
Phenacite	500°		(70)
Phillipsite	200–500°		(?103)
Alteration of			(40)
Pitchstone			
Action of water on			(41, after ignition)
Dehydration of			(97)
Plagioclase, alteration of			(145)
Potassium aegirine	470°		(84)
Potassium analcite	360–400°		(?79)
Potassium disilicate	200–1041°		(89)
Potassium disilicate monohydrate	280–405°		(89)
"Potassium faujasite"	450°		(?78)
Potassium feldspar (See adularia, microcline, and orthoclase)			
Alteration of			(119), (133), (145)
Potassium hydrogen disilicate	420–515°		(89)
Potassium metasilicate	610–996°		(89)
Potassium metasilicate hemihydrate	370–610°		(89)
Potassium metasilicate monohydrate	200–370°		(89)
Potassium natrolite	200°		(56)
Potassium silicate, hydrous	<Red		(18)
Powellite	395°		(116)
Prehnite, alteration of			(40), (41, after fusion)
"Prokaolin"			(99), (132), (135)
Pumice			(65)
Pyrophyllite	250°(156)	540°(145)	(78), (?84), (?85), (?91), (?138), (141), (142), (144), (145), (155), (156)
Alteration of			(138, attempted)
Pyroxene	395°(115)	550°(48)	(5, hedenbergite), (14, Mg), (24, rhodonite), (39), (48, diopside), (75, aegirine-augite), (85, hedenbergitic augite), (115, diopside)
Alteration of			(5), [(26), (77), augite]

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Quartz	100°(4, 64)	600°(89) 750°?(100)	(1), (3), (4), (5), (?7), (8), (11), (12), (13), (18), (19), (23), (34), (36), (?36a), (42), (48), (49), (57), (59), (64), (68), (71), (72), (74), (75), (78), (81), (85), (89), (91), (100), (101), (104), (156)
As a reagent			(22), (121), (137), (137, fused silica), (148), (154)
Solubility and transport of silica			(62), (63), (64), (68), (75), (90), (111), (112), (113), (115), (116), (117), (118), (129), (130), (136), (138), (139), (146), (147), (149)
Solubility curves			(Fig. 11, page 691)
Rhodonite	Red; >650°?		(24)
Alteration of			(24)
$2R''O \cdot SiO_2$	Red		(24)
Sandstone, alteration of			(26)
Sanidine, alteration of			(26), (31), (56, attempted)
Sassolite	Room		(104)
Scapolite	470°		(?85)
Alteration of			(40)
Scheelite	380°		(116)
Scolecite	<200°(10)	220°(40)	(?10), (?40), (43)
Alteration of			(10), (40), (40, after fusion), (43)
Sericite	225°(All)	350°(156)	(?103), (124), (155), (156)
Serpentine	300°(101)	475°(109)	(101, amianthus), (?109), (146)
Alteration of			(41, after ignition), (92), (94)
Silica, crystalline hydrated	180°(8)	320°(101)	(?8), (?101)
Silicon	Low red		(16)
Sillimanite	540°		(?141)
Alteration of			(138, attempted)
$5SiO_2 \cdot 3H_2O$	310–320°		(?101)
Sodalite	200°(40)	500°(46)	(40), (46), (60)
Alteration of			(31), (41), (56)
"Sodium anorthite"	Fusion		(56)
Alteration of			(56)
Sodium cancrinite	500°(All)	530°(59)	(50), (59), (70)
Sodium disilicate	300°		(83)
Sodium metasilicate	500°		(83)
Critical temperatures of solutions of			(149)
Sodium thomsonite	500–530°(59)		(59), (66), (67)
Spessartite	Cherry red		(25)
Spinel	Red (15, 27, 53) 550°(77)		(15), (27), (53), (77)
Alteration of			(75)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Spodumene, alteration of			(31), (40), (103)
Steatite	200°	350°?	(?80)
Stilbite		450°	(78)
Alteration of			(41, after fusion)
Strontianite		365°	(115)
Talc	200°	350°?	(?80)
Tephroite	365°(115)	>650°?(24)	(24), (115)
Reaction of			(24)
Thomsonite		200°	(?103)
Alteration of			(40)
Thomsonite, sodium		500–530°(59)	(59), (66), (67)
Topaz		500°	(38)
Alteration of			(41)
Tourmaline			(?131)
Tremolite		400°	(76)
Alteration of			(41, after fusion), (76, de- and rehydration)
Tridymite	175°(8)	520°(71)	(8), (9), (12), (?28), (34), (?39), (42), (57), (71), (75), (81, changed to quartz), (85), (?100), (104)
Unidentified crystals			(7), (31), (40), (54), (55), (70), (77), (104), (141), (148)
Bundle-like aggregates			(75), (85, No. 10)
Columns			(26)
Crystalline powder			(52), (75)
Globulites			(23), (46), (54), (84)
Hexagonal plates			(75), (88), (104)
Hydrous calcium silicate			(?110)
Hydrous silicate			(109)
Isometric			(23), (31), (39), (75), (85)
Microlites			(91)
Monoclinic			(85), (104)
Needles			(23), (26), (54, 3 kinds), (71), (75), (85, 3 kinds), (88), (104), (137)
Orthorhombic			(85)
Radial clusters			(71)
Rectangular tablets			(33)
Red Fe-bearing plates			(75)
Rods			(85), (88)
Silicate			(85, No. 11)
Spherulites			(104)
Uniaxial negative			(104)
Willemite	365°(115)	600°(120)	(115), (120, fluorescent), (129), (136)

Mineral	T. Min. (Ref.)	T. Max. (Ref.)	References
Wollastonite.....	210°(86, CO_2)	425°(73) Red (28)	(?5), (28), (?39), (52), (73), (86), (115)
Alteration of....			(26), (31), (41, after fusion)
Xonotlite.....	180–200°(122)		(122), (148), (?154)
Zeolites, alteration of.....			(10)
Zeolites, not specifically identified..	110°(91)	430°(91)	(40), (41), (91, 6 kinds), (103), (106), (?140), (155)
Zinc silicate.....	300°		(?101)
Zircon.....	Red		(55)
Zr-Al silicate, hydrous.....	Red		(55)
"Zunyite".....	470°		(85)

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